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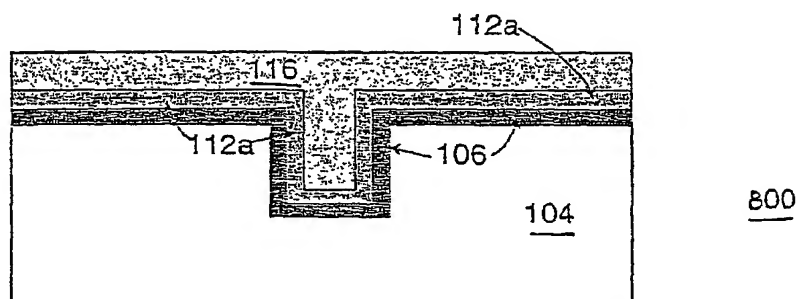
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(54) Title: METHODS FOR REGULATING SURFACE SENSITIVITY OF INSULATING FILMS IN SEMICONDUCTOR DEVICES



(57) Abstract: Methods are provided for regulating surface sensitivity of the deposition of silicon dioxide films that can permit the deposition of high quality silicon dioxide films for use in shallow trench isolation. By the use of super low ozone concentrations to deposit a seed layer having low ozone content, the subsequent deposition of high-quality, high ozone films can be facilitated, without the appearance of defects that can appear during conventional high ozone film deposition. Controlling the ozone concentration during seed layer deposition, the thickness of the seed layer, the rates of deposition of the high ozone film, deposition temperature and ozone concentration of the high ozone film, the resulting SiO<sub>2</sub> film can exhibit desired properties. Semiconductor thin films according to the methods of this invention can be made thinner than conventional TEOS/ozone films, permitting the manufacture of integrated circuit devices having smaller dimensions. Additionally, methods are presented for increasing the surface sensitivity of deposition of SiO<sub>2</sub> films on semiconductor wafers having different materials thereon. By increasing surface sensitivity, differential growth rate of SiO<sub>2</sub> on nitride, thermal oxide and silicon can be adjusted to provide increased planarity of the deposited SiO<sub>2</sub> layer and can result in reduced dimensions of SiO<sub>2</sub> layers to achieve planar surfaces and thereby can decrease manufacturing cost and device size.

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## METHODS FOR REGULATING SURFACE SENSITIVITY OF INSULATING FILMS IN SEMICONDUCTOR DEVICES

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### BACKGROUND OF THE INVENTION

#### Field of the Invention

This invention comprises methods for manufacturing semiconductor devices, more particularly to processes for depositing silicon dioxide films by chemical vapor deposition. More specifically, this invention includes methods for regulating the surface sensitivity of deposition of thin films depending on the types of substrates and the desired characteristics of films to be deposited.

#### Discussion of Related Art

Device density in integrated circuits has almost doubled in the past 2 years. With this increase in device density, the need to effectively isolate transistors as well as conductive layers has become increasingly important to the high-yield production of highly reliable integrated circuit devices. It is well known that silicon dioxide ( $\text{SiO}_2$ ) dielectric films can be deposited using chemical vapor deposition ("CVD") with good conformality from the precursor tetraethylorthosilicate and a mixture of ozone and oxygen ("TEOS/ $\text{O}_3$ ") at relatively low temperatures. Temperatures can be about 400° C, and the deposition can be carried out at either atmospheric pressure (an "APCVD"

process) or sub-atmospheric pressure (a "SACVD" process).

It is also known that the ratio of  $O_3$  to TEOS during the dissociation and deposition reactions can affect the film quality as well as the deposition profile. In forming  $SiO_2$  films by TEOS/ $O_3$  processes, the growth rate and quality of the film can depend on the nature of the substrate onto which the film is deposited. This dependency is herein termed "surface dependency" or "surface sensitivity." Surface sensitivity can be characterized by inconsistent and variable deposition rates on different substrates, and of variable surface roughness and quality of the deposited film as process conditions are varied.

Surface sensitivity can be observed for several types of substrates, including silicon dioxide formed using thermal oxidation, TEOS/ $O_3$  processes, or TEOS/ $O_2$  plasma enhanced CVD ("PECVD") processes. Furthermore,  $SiO_2$  can be doped with phosphorous to make phosphorous doped silicate glass ("PSG"), boron to make boron doped silicate glass ("BSG") or a combination of PSG and BSG, as well as spin-on glass ("SOG"). Deposition of  $SiO_2$  on these types of substrates can also show surface sensitivity. Surface sensitivity can also be observed for deposition on nitride layers, including silicon nitride and silicon oxynitride.

Some methods for eliminating or reducing surface dependency of TEOS/ $O_3$  deposition have been described. Most of the solutions either require additional equipment and/or pre-treatment steps. Maeda (U.S. Patent No:

5,051,380; the “380” patent, incorporated herein fully by reference), described a two-layer CVD-SiO<sub>2</sub> film, where a first layer of SiO<sub>2</sub> is deposited using a concentration of O<sub>3</sub> at 0.5% by volume and a temperature of 400° C, and a second layer of TEOS/O<sub>3</sub> is deposited using higher O<sub>3</sub> concentration.

5           It is known that films produced with low ozone can have good conformality in that they can conform to the shapes of the substrates upon which they are deposited. However, the quality of low ozone films is known to be poor when compared to high ozone films. Low ozone films tend to have more moisture and/or lower density, resulting in possible reliability problems  
10           in the future operation of the integrated circuit, and therefore tend to have poorer quality. In contrast, high quality films are characterized by lower moisture composition and higher densities than low quality films.

          Problems resulting from surface sensitivity can be observed in uneven deposition of SiO<sub>2</sub> films for shallow trench isolation. Shallow trench isolation  
15           (“STI”) is a method for electrically separating active devices on a semiconductor wafer by inscribing a groove or trench in the substrate and then filling the trench with a dielectric material, such as SiO<sub>2</sub>. It can be desirable to have semiconductor features such as oxide layers or nitride layers on the substrate. The trenching process can result in the existence of several different  
20           types of semiconductor materials being exposed to the conditions of SiO<sub>2</sub> deposition: bare silicon in the trench, and oxide and/or nitride layers on the top

surface, if present. During deposition of  $\text{SiO}_2$ , it can be desired to cover all of the features on the semiconductor wafer with an even layer of  $\text{SiO}_2$ . However, as will be described below, the deposition rates and the quality of the  $\text{SiO}_2$  on the different types of semiconductor materials can be very different.

5            Figures 1a - 1g depict prior art shallow trenches and conventional methods for providing gap filling with oxide dielectric material. These structures are also indicative of interlevel or pre-metal dielectric ("ILD") and intermetal dielectric ("IMD") structures. They are made up of narrow gaps cut out of a layer of material. For the STI structure, the materials are deposited in  
10            trenches cut in the base wafer substrate material. Other structures are made up of gaps between polysilicon and polycide for ILD, and between IMD structures made of the metal used for interconnects.

             Figure 1a depicts a prior art semiconductor wafer **100** having a silicon substrate **104**, trench **108** and having a layer of low ozone  $\text{SiO}_2$  **112** deposited  
15            on the walls of trench **108**.

             Figure 1b depicts a prior art semiconductor wafer **100** comprising substrate **104**, and having a trench filled with low ozone  $\text{SiO}_2$ . Because low ozone  $\text{SiO}_2$  layer **112** is conformal, it creates a weak seam **114**, which is a site of defects in the dielectric material. Among other things, the defects result in  
20            decreased electrical isolation and decreased device reliability.

             Figure 1c depicts a prior art semiconductor wafer **100** comprised of a

silicon substrate **104** and trench **108** partially filled by a high ozone flow-like film **113**. The flow-like quality of the film provides rounded contours of the film in the trench **108**.

Figure 1d depicts a prior art semiconductor wafer **100** as shown in  
5 Figure 1c, where the trench has been completely filled with high-ozone SiO<sub>2</sub> film **113**. No weak seam is present.

Figure 1e depicts a prior art semiconductor wafer **100** comprising a silicon substrate **104** and having a trench lined with a layer of thermal oxide **106**. The trench has been filled with high-ozone SiO<sub>2</sub>, but exhibits numerous  
10 defects, including voids **115** and surface roughness **117**.

According to the '380 patent, there was an irreducible minimum thickness of the first layer of TEOS/O<sub>3</sub> film deposited at low ozone concentration. In a publication by the same group (Fujino et al. *J. Electrochemical Society* 138(2):550-554 (1991), the minimum thickness of the  
15 low ozone TEOS film was considered to be 1000 Å. With trench structures becoming smaller, for example, less than 2000 Å (0.2 μm), a trench having a 1000 Å thick layer of low ozone TEOS cannot then be filled with high quality oxide derived from high ozone deposition of TEOS. The high ozone oxide is needed to provide a high degree of electrical stability to the deposited film.  
20 Thus, for future requirements to fill gaps of less than 0.18 μm, there would be insufficient space available in the trench after the deposition of the low ozone

film for the better quality, high ozone film.

Figure 1f depicts a prior art semiconductor wafer **100** as shown in Figure 1e, comprising a silicon substrate **104**, a trench having a liner of thermal oxide **106**, and having a layer of low-ozone SiO<sub>2</sub> **112** made according to prior art methods. The remainder of the trench has been filled with high-ozone SiO<sub>2</sub> **116**. The thickness of the low-ozone SiO<sub>2</sub> is shown as 1000 Å.

As device geometries are reduced below sub-quarter micron dimensions, void-free gap filling using these methods are difficult because the film type deposited within the trenches would dominantly be comprised of the low O<sub>3</sub> type of film. Being conformal in nature, the low O<sub>3</sub> film tends to fill gaps from the sides of the trench, which can result in the formation of weak seams and voids as the gap filling reaches completion. The weak seam allows surface impurities to more readily migrate through the film, possibly to the electrically active regions of the integrated circuit components. Thus, a seam or any other structural defect which can allow impurity migration is undesired. Alternatively, if the gap is only filled with high ozone oxide, surface sensitivities result in poor gap filling, weak seams, voids and/or rough surfaces. High ozone TEOS films deposited on thermal oxide do not fill narrow gaps. This can be due to film growth on the sharp corner areas of the structure being faster than the deposition on more planar surfaces. The enhanced growth rate at the edges can cause a void to be formed as the gap becomes filled with



dielectric material. Both the structural defects and voids can result in enhanced diffusion of impurities.

Figure 1g depicts a semiconductor device **100** having a narrow trench. Silicon substrate **104** has a liner oxide layer of thermal oxide **106** and a layer of low-ozone SiO<sub>2</sub> **112** is shown, having a thickness of about 1000 Å. Because the trench width is equal to or less than twice the thickness of the low ozone layer, i.e., 2000 Å in this case, the low-ozone layer **112** completely fills the gap, resulting in the formation of a weak seam **114** or void. Subsequent deposition of high-ozone SiO<sub>2</sub> **116** provides no further filling of the trench. Therefore, the problems solved using the low-high ozone method may not provide satisfactory filling of trenches having narrow dimensions of less than 2000 Å. Thus, for future requirements of filling gaps of less than either 0.18 or 0.15 μm, there would be insufficient space available in the trench after the deposition of the low ozone film for the better quality, high ozone film.

Another problem associated with semiconductor device manufacture is the problem of poor planarity of semiconductor devices having SiO<sub>2</sub> surfaces. Because semiconductor devices typically have several types of films, including SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, polysilicon, polycide and conductor metals in combination with narrow gap type features, the growth of TEOS ozone on the surfaces can vary. For example, a good quality high ozone film can have a higher growth rate on silicon than on either silicon dioxide or on silicon nitride (Elbel et al.

*Symposium on VLSI Technology Digest of Technical Papers* 21.2:208-209 (IEEE 1998), incorporated herein by reference). This results in thinner layers being deposited on nitride than on silicon and an uneven topography of the semiconductor wafer surface. To permit small device dimensions to be used, wafers may need to be planarized using chemical mechanical polishing (“CMP”). The need for CMP increases the time, cost, and equipment needed for semiconductor manufacture.

A method that takes advantage of differential deposition rate is described in the above-identified reference by Elbel et al. By providing a layer of nitride on the surface of the wafer, and keeping the trenches free of nitride (i.e., bare silicon), subsequent deposition of TEOS/O<sub>3</sub> results in a differential deposition, with a thicker layer of SiO<sub>2</sub> being deposited on silicon than on nitride in the same time period. Thus, by regulating the deposition time, the differences in thicknesses of the SiO<sub>2</sub> can result in a relatively even top surface.

Figure 2a depicts a semiconductor device **200** made according to a prior art method described immediately above. Wafer **200** comprises a silicon substrate **104** having a trench inscribed therein for shallow trench isolation. The top surface of the wafer has layers of nitride **118** deposited thereon. The trench has been filled with high ozone SiO<sub>2</sub> film **116** so that the top surface **119** of the SiO<sub>2</sub> film is nearly planar. Unfortunately, the interface between the high-ozone SiO<sub>2</sub> layer **116** and silicon substrate **104** can have defects due to

thermal stresses and lattice discontinuity.

Figure 2b depicts a semiconductor device **200** made according to the prior art methods as shown in Figure 2a after having been annealed at a temperature of about

5 700° C for about 1 hour to form a layer of liner oxide **122**. This annealing step can provide a better interface between high-ozone SiO<sub>2</sub> layer **116** and the silicon substrate **104** than is made using the method shown in Figure 2a.

Figure 2c depicts a semiconductor wafer **200** manufactured using methods of the prior art. Wafer **200** comprises a silicon substrate **104** and a trench inscribed therein for shallow trench isolation. Unlike the method illustrated in Figure 2b, in this method, a layer of liner oxide **122** is formed prior to deposition of a high-ozone SiO<sub>2</sub> layer **116**. After formation of liner oxide **122**, the trench is filled with TEOS/O<sub>3</sub> **116**. As with other prior art methods for depositing high-ozone SiO<sub>2</sub> on thermal oxide, defects are present in the SiO<sub>2</sub> layer **116**. The defects include pores **115** and surface roughness **117**.

Figure 2d depicts a prior art method for providing low-ozone SiO<sub>2</sub> in a narrow trench of future integrated circuits. The trench is depicted having a width of about 0.18 μm. Wafer **200** comprises a silicon substrate **104** having a trench lined with a layer of thermal oxide **122**, and nitride layers **118** formed on the top surface of silicon wafer **200**. Subsequently, a film of low-ozone

SiO<sub>2</sub> **112** having a thickness of about 1000 Å was deposited over the wafer. Because the low ozone SiO<sub>2</sub> layer is about 1000 Å in thickness, the gap is shown completely filled with low ozone SiO<sub>2</sub> and a weak seam **114** is present. Further, because the rate of deposition of SiO<sub>2</sub> on thermal oxide is low, the  
5 surface **119** of SiO<sub>2</sub> layer **112** is uneven, there being a depression in the trench. Because the low ozone film **112** fills the trench, there is no space in the trench available for high ozone film. Because there is no room in the trench for high ozone film, the overall film quality of the trench-filling dielectric material is not suitable for future integrated circuit uses.

10 Therefore, the prior art methods for manufacturing shallow trench isolation have not solved the problems associated with narrow gap filling with high quality oxide.

### SUMMARY OF THE INVENTION

15 An object of this invention is to provide CVD methods for deposition of high-quality silicon dioxide films on a variety of different substrates having different surface sensitivities.

Another object of this invention is to develop methods for depositing silicon dioxide films using CVD which have reduced surface sensitivity using  
20 “seed” layers of silicon dioxide being sufficiently thin to be useful for future integrated circuit fabrication.

Another object of this invention is to provide methods for reducing the thickness of the seed layer, to permit the filling by high ozone TEOS/O<sub>3</sub> of semiconductor gaps of less than 0.25  $\mu\text{m}$ .

5 An additional object of this invention is to use flow-like high O<sub>3</sub> TEOS/O<sub>3</sub> materials to permit improved, low-defect filling of gaps having dimensions of less than 0.18  $\mu\text{m}$ .

A further object of this invention is to provide methods for optimizing the deposition of SiO<sub>2</sub> on different substrate surfaces to achieve surface topography that decreases the need for any type of planarization.

10 In certain embodiments, methods are provided in which a first film of CVD-TEOS/O<sub>3</sub> can be deposited at atmospheric pressure as a seed layer made using a first, low O<sub>3</sub> concentration, followed by a the deposition of a second CVD-TEOS/O<sub>3</sub> layer made using a higher concentration of ozone than the first ozone concentration. By varying the conditions of deposition, it is possible to  
15 vary the deposition rates and quality of the resulting films. We evaluated the relationships between ozone concentrations, deposition rates and seed layer thicknesses on different substrates over a broad range of low ozone concentrations, and the effects of changes in the deposition temperature on the surface sensitivity for oxide deposition.

20 We have unexpectedly found that decreasing the concentration of ozone in the seed layer to well below the concentrations previously used

(below 10 gm/m<sup>3</sup>), a seed layer can be formed that is sufficiently thin to permit the deposition of high quality, high-ozone SiO<sub>2</sub> in shallow trenches having gap dimensions of less than 0.18 μm. We have also unexpectedly found that either lowering or raising the deposition temperature compared to conventional methods can decrease the surface sensitivity of SiO<sub>2</sub> deposition. By regulating the deposition rate of TEOS/O<sub>3</sub> films, the surface sensitivity can be adjusted to suit particular requirements of semiconductor manufacture. In certain embodiments of this invention, it can be desirable to increase surface sensitivity. By selecting high ozone concentrations, increased temperatures, or reduced deposition rates, the growth rate of silicon dioxide on different types of semiconductor materials can be adjusted to suit particular needs.

By selecting deposition conditions based on the desired film quality, substrates, and the desired film thickness, the methods of this invention can improve the quality of film used in semiconductor manufacturing, can improve manufacturing efficiency, and can provide high-quality gap filling for shallow trenches having the small dimensions necessary for the manufacture of future integrated circuits. The methods of this invention are useful for interlayer dielectric and intermetal dielectric applications.

**BRIEF DESCRIPTION OF THE FIGURES**

The invention will be described with respect to the particular embodiments thereof. Other objects, features, and advantages of the invention will become apparent with reference to the specification and drawings in which:

5           Figures 1a - 1g depict shallow trench isolation of prior art semiconductors.

Figure 1a depicts a shallow trench with a thin layer of low ozone oxide according to methods of the prior art.

10           Figure 1b depicts a prior art shallow trench as shown in Figure 1a after the low ozone oxide layer has filled the trench.

Figure 1c depicts a shallow trench isolation of a prior art semiconductor with a thin layer of high ozone oxide.

15           Figure 1d depicts a shallow trench isolation of a prior art semiconductor shown in Figure 1c after the high ozone oxide layer has filled the trench.

Figure 1e depicts a prior art shallow trench filled with high ozone oxide deposited on thermal oxide within the trench.

20           Figure 1f depicts a prior art shallow trench having a layer of thermal oxide and deposition of a layer of low ozone oxide, followed by a layer of high ozone oxide.

Figure 1g depicts the problem associated with using conventional low

ozone deposition to attempt to fill a narrow trench for shallow trench isolation of future semiconductor devices.

Figures 2a - 2d depict prior art shallow trench isolation using differential deposition rates.

5           Figure 2a depicts a prior art shallow trench of silicon and a top surface of nitride after the trench has been filled with a TEOS/O<sub>3</sub> film.

Figure 2b depicts a prior art shallow trench as depicted in Figure 2a after annealing to form a layer of liner oxide in the trench.

10           Figure 2c depicts a prior art shallow trench as depicted in Figure 2a, additionally having a liner oxide layer of thermal oxide formed in the trench prior to filling the trench with SiO<sub>2</sub>.

Figure 2d depicts a prior art method for filling a trench lined with a layer of thermal oxide and subsequently filled with low-ozone SiO<sub>2</sub>.

15           Figure 3 is a graph of the relationship between ozone concentration and TEOS/O<sub>3</sub> deposition rate for substrates of silicon, nitride and thermal oxide according to an embodiment of this invention.

20           Figure 4 is a graph of the relationships between ozone concentration and the thickness of a super low ozone ("SLO") layer necessary to achieve a growth rate ratio with respect to that on silicon of 0.9 on nitride and thermal oxide according to an embodiment of this invention.

Figure 5a depicts the relationships between the thicknesses of SLO



layers deposited at an ozone concentration of 1 gm/m<sup>3</sup> and growth rate ratios of high ozone SiO<sub>2</sub> on nitride and thermal oxide according to an embodiment of this invention.

Figure 5b depicts the relationships between the thicknesses of SLO  
5 layers deposited at an ozone concentration of 3 gm/m<sup>3</sup> and growth rate ratios of high ozone SiO<sub>2</sub> on nitride and thermal oxide according to an embodiment of this invention.

Figure 6 depicts the relationship between deposition temperature and growth rate ratio of TEOS/O<sub>3</sub> films on nitride according to an embodiment of  
10 this invention.

Figure 7 depicts the relationships between SLO layer thicknesses, growth rate ratios for thermal oxide and deposition temperature for SiO<sub>2</sub> films deposited according to an embodiment of this invention.

Figure 8 depicts a semiconductor wafer of an embodiment of this  
15 invention, wherein a narrow trench is filled with liner oxide, a layer of SLO and high ozone TEOS/O<sub>3</sub>.

Figure 9 depicts a semiconductor wafer of an embodiment of this invention having a nitride layer and a narrow trench having a liner oxide layer, a layer of SLO, and high-ozone TEOS/O<sub>3</sub>.

Figure 10a is a graph that depicts the relationships between the  
20 deposition rate and layer thickness on the growth rate ratio for high ozone films

of an embodiment of this invention grown on nitride at a temperature of 400°C.

Figure 10b is a graph that depicts the relationships between the deposition rate and layer thickness on the growth rate ratio for high ozone films of an embodiment of this invention grown on nitride at a temperature of 350°C.

5        Figure 10c is a graph that depicts the relationships between the deposition rate, layer thickness and temperature on the growth rate ratio for high ozone films of an embodiment of this invention at temperatures of 350° C and 400°C.

10        Figure 11 is a graph that depicts the effects of SLO seed layers on the temperature dependency of high ozone SiO<sub>2</sub> film growth.

Figure 12a - 12c depict prior art semiconductor wafers having multiple types of surface materials.

Figure 12a depicts a prior art wafer having silicon substrate, an oxide layer, a nitride layer and a thin layer of SiO<sub>2</sub> deposited over the entire wafer.

15        Figure 12b depicts a prior art wafer as shown in Figure 12a with a thicker layer of SiO<sub>2</sub> deposited over the wafer, showing non-planarity over different types of underlying layer materials.

Figure 12c depicts a prior art wafer as shown in Figures 12a and 12b with a thicker layer of SiO<sub>2</sub> compared to the layer depicted in Figure 12b.

20        Figure 13 depicts a semiconductor wafer made according to an embodiment of this invention, in which the SiO<sub>2</sub> layer was deposited at a

relatively low temperature.

Figure 14 depicts a semiconductor wafer made according to an embodiment of this invention, in which the SiO<sub>2</sub> layer was deposited at a higher temperature than that used for the wafer depicted in Figure 13.

5           Figures 15a - 15c depict a semiconductor device having TEOS/ozone film deposited according to an embodiment of this invention.

Figure 15a depicts a semiconductor device prior to deposition of TEOS/ozone film.

10           Figure 15b depicts a semiconductor device as in Figure 15a after a TEOS/O<sub>3</sub> layer was deposited according to an embodiment of this invention at an ozone concentration of 120 gm/m<sup>3</sup>.

Figure 15c depicts a semiconductor device of as in Figure 15a, after a TEOS/O<sub>3</sub> layer was deposited according to an embodiment of this invention at an ozone concentration of 250 gm/m<sup>3</sup>.

15           Figures 16a - 16b are photographs of semiconductor wafers having trenches filled with TEOS/ozone according to an embodiment of this invention.

Figure 16a is a photograph of a wafer having a shallow trench and a layer of silicon nitride, the trench being filled with TEOS/ozone according to an embodiment of this invention.

20           Figure 16b is a photograph of a wafer having a shallow trench and a layer of silicon nitride and a liner oxide layer in the trench, the trench being

filled with TEOS ozone film according to an embodiment of this invention.

Figures 17a and 17b depict a method for providing super high ozone  $\text{SiO}_2$  films of one embodiment of this invention.

Figure 18 depicts a scanning electron micrograph of a wafer having  
5 shallow trenches, nitride caps and a super high ozone  $\text{SiO}_2$  film of an  
embodiment of this invention within the trenches.

### DETAILED DESCRIPTION

The general methods used to form films according to the methods of  
10 this invention comprise atmospheric pressure chemical vapor deposition  
("APCVD"), although other types of CVD deposition also can be used.  
Depositions can be carried out using ozone generated from oxygen gas and a  
precursor of  $\text{SiO}_2$ , such as by way of example, tetraethylorthosilicate  
("TEOS"). However, any suitable precursor for the formation of  $\text{SiO}_2$  can be  
15 used. The conditions of deposition can be carefully adjusted to achieve the  
desired films of this invention. The conditions that are especially useful include  
ozone concentration, precursor flow rate, deposition rate, deposition  
temperature, thickness of a seed layer of oxide, and the type of substrate.

The formation of a seed layer of super low ozone ("SLO")  $\text{SiO}_2$  can  
20 increase the growth rate ratio of subsequently deposited high ozone  $\text{SiO}_2$  films.  
Altering the temperature of deposition and the deposition rates of high ozone

SiO<sub>2</sub> can also affect surface sensitivity. By combining the use of a SLO layer and closely controlling the conditions for high ozone film deposition, the surface sensitivity of film deposition can be closely regulated to achieve desired film properties such as water content, film density, gap filling properties, mechanical stresses, interface quality in between film materials, and the electrical properties of the resulting low dielectric constant SiO<sub>2</sub> films.

#### **I. Methods for Depositing SiO<sub>2</sub> Using Super Low Ozone Seed Layers**

According to certain embodiments of this invention, a first layer of SiO<sub>2</sub>, herein termed “super low-ozone” or “SLO” SiO<sub>2</sub>, can be deposited on a substrate, followed by another layer of SiO<sub>2</sub>, made at a higher ozone concentration, herein termed “high ozone” SiO<sub>2</sub>, than the first SLO SiO<sub>2</sub> film. The thickness of low ozone TEOS/ozone can be relatively small, leaving sufficient room for the remainder of the trench to be filled with high ozone TEOS ozone dielectric film. Novel features of embodiments of this invention include selecting lower concentrations of ozone for the low-ozone film than have been previously used. By decreasing the concentration of ozone, for example, to the range of about 0.01 gm/m<sup>3</sup> to about 10 gm/m<sup>3</sup> during deposition, the thickness and adherence properties of subsequently deposited high ozone films can be regulated to suit the specific application needs. In other embodiments of this invention, ozone concentrations in the range of

about  $0.05 \text{ gm/m}^3$  to about  $10 \text{ gm/m}^3$  are suitable, and for other embodiments, ozone concentrations in the range of about  $0.1 \text{ gm/m}^3$  to about  $5 \text{ gm/m}^3$  are suitable. In yet other embodiments, ozone concentrations of  $0.5 \text{ gm/m}^3$  or about  $3 \text{ gm/m}^3$  can be desirable.

5           Regulating the temperature of deposition of the super low-ozone film can also provide alternative methods for adjusting the deposition and quality of high-ozone films. Any temperature in the range where  $\text{SiO}_2$  deposition proceeds at a desirable rate and wherein the underlying film remains intact can be used. Temperatures generally useful can be in the range of about  $300^\circ \text{C}$  to about  $800^\circ$ , alternatively about  $350^\circ \text{C}$  to about  $650^\circ \text{C}$ , and in other  
10           embodiments, about  $375^\circ \text{C}$  to about  $600^\circ \text{C}$ .

By the use of the low ozone concentrations of embodiments of this invention, the thickness of a SLO films can be decreased to well below those possible using prior art methods. SLO films can be made in any thickness  
15           desired, given any constraint on the size of a feature or gap to be filled. For relatively narrow gaps, SLO films having thicknesses in the range of about  $100 \text{ \AA}$  to about  $1000 \text{ \AA}$  can be desired, in other embodiments, SLO films having thicknesses in the range of about  $200 \text{ \AA}$  to about  $700 \text{ \AA}$  can be desired, in yet other embodiments, films can have thicknesses in the range of about  $300 \text{ \AA}$  to  
20           about  $600 \text{ \AA}$ , and in yet other embodiments, the thicknesses can be in the range of about  $400 \text{ \AA}$  to about  $500 \text{ \AA}$ .

After deposition of the SLO seed layer, a second layer, having a thickness sufficient to provide a desired total thickness of  $\text{SiO}_2$  can be formed. This second layer can be used to fill gaps in shallow trenches. By way of example, the second layer can have a thickness in the range of about 1000 Å to about 10,000 Å or thicker, depending upon the application.

High-ozone films generally can be made using ozone concentrations in the range of about 20  $\text{gm/m}^3$  to about 120  $\text{gm/m}^3$ , or even higher. In other embodiments of this invention, the high ozone layer can be made using super high ozone ("SHO") concentrations in the range of about 120  $\text{gm/m}^3$  to about 320  $\text{gm/m}^3$ , and in another embodiment, about 160  $\text{gm/m}^3$ .

#### **A. Seed Layer Deposition to Reduce Surface Sensitivity**

In one series of embodiments of this invention, a seed layer of oxide film is deposited using  $\text{O}_3$  concentrations in the range of about 1  $\text{gm/m}^3$  to about 5  $\text{gm/m}^3$  and a seed layer thickness of about 100 Å or more. In certain other embodiments of this invention, a thickness of about 600 Å can be desirable. Subsequently, non-doped silicate glass ("NSG") or other type of  $\text{SiO}_2$  can be deposited using high-ozone TEOS/ $\text{O}_3$  methods.

Table 1 shows some process variables for deposition of low ozone and high ozone TEOS/ $\text{O}_3$  films of this invention. The TEOS flow rate in nitrogen is given in standard liters per minute (SLM).

**Table 1**  
**Deposition Variables for TEOS/Ozone Films**

5	<b>Process Variable</b>	<b>Super Low Ozone</b>	<b>High Ozone</b>	<b>Super High Ozone</b>
	<b>Deposition Temp. (C°)</b>	300 - 800	300 - 800	300 - 800
10	<b>O<sub>3</sub> Concentration (gm/m<sup>3</sup>)</b>	0.01 - 20	20 - 120	120 - 320
15	<b>TEOS Flow Rate (N<sub>2</sub> Carrier Gas; SLM)</b>	0.1 - 10	0.1 - 10	0.1 - 10

We have unexpectedly found that using ozone concentrations either below or above those conventionally used, the growth rate ratio of SiO<sub>2</sub> on nitride compared to that on silicon can be as low as about 0.2, and as high as about 1.0. By varying the conditions of SiO<sub>2</sub> deposition, the quality and thickness of SiO<sub>2</sub> layers can be controlled.

### EXAMPLES

The following examples are intended to illustrate, without limitation, certain embodiments of this invention. Workers of ordinary skill in the art can develop other variations of the embodiments of this invention without departing from the scope of this invention. All of those other variations are



considered to be part of this invention.

### Example 1: Effect of Seed Layer Ozone Concentration on Surface Sensitivity

In one experiment shown in Table 2, growth rate ratio was measured for NSG films grown at 120 gm/m<sup>3</sup> ozone concentration on SLO layers having different seed layer thicknesses grown at different ozone concentrations. The temperature of deposition was 400° C.

**Table 2**  
**Effect of Ozone Concentration and Seed Layer Thickness**  
**on Growth Of SiO<sub>2</sub> Films**

O <sub>3</sub> (gm/m <sup>3</sup> )	Seed Layer Thickness (Å)		Film Thickness (Å)		Growth Rate Ratio	Growth Rate Ratio
		Si	Thermal Oxide	Nitride	Thermal Oxide/Si	Nitride/Si
1	350	5737	5335	5437	0.93	0.95
3	500	5983	5565	5754	0.93	0.96
5	600	6132	5393	6063	0.88	0.98

Table 2 shows that as the ozone concentration increased from 1 gm/m<sup>3</sup> to 5 gm/m<sup>3</sup>, the thickness of the resulting seed layer increased from 350 Å to 600 Å. The thickness of deposited film on silicon (Si) increased from 5737 Å to 6132 Å, but the growth rate on thermal oxide was only slightly different from

the growth rate on silicon. The growth rate of  $\text{SiO}_2$  on nitride increased from 5437 to over 6000 Å. The growth rate of  $\text{SiO}_2$  on thermal oxide compared to the growth rate on silicon (growth rate ratio) decreased slightly (from 0.93 to 0.88), whereas the growth rate ratio for nitride increased from 0.95 to 0.98.

5           Figure 3 is a graph of ozone concentration (in % volume of ozone/volume of oxygen) and the rate of deposition of  $\text{SiO}_2$  films from TEOS/ $\text{O}_3$  in nm/min. At ozone concentrations below 1 volume % (20 gm/m<sup>3</sup>), the rate of deposition of  $\text{SiO}_2$  films was nearly the same for the three types of substrates, silicon ( $\Delta$ ), silicon nitride (\*), and thermal oxide (x). However, at  
10           ozone concentrations above about 1 volume %, the rates of deposition of  $\text{SiO}_2$  on all three substrates decreased with increasing ozone concentration. The deposition rate on Si decreased the least, the growth rate decrease was greater for nitride, and the growth rate decreased the most for films grown on thermal oxide.

15           Figure 4 is a graph depicting the effects of ozone concentration (in gm/m<sup>3</sup>) on the thickness of a super low ozone (SLO) TEOS layer necessary to achieve a growth rate ratio of 0.9 (compared to the growth rate on silicon) for thermal oxide and nitride. For  $\text{SiO}_2$  growth on thermal oxide ( $\square$ ), the thickness of SLO layer was greater than the thickness required for growth on nitride ( $\blacklozenge$ ).  
20           Furthermore, increasing the ozone concentration increased the thickness of SLO needed to achieve a growth rate ratio of 0.9. To achieve a growth rate

ration of 0.9 using an ozone concentration of  $10 \text{ gm/m}^3$  (0.5% volume:volume) the thickness of the layer of SLO was about  $800 \text{ \AA}$ .

5                   **Example 2: Effect of Seed Layer Thickness on Surface Sensitivity**

In another series of studies, we determined the effects of SLO layer thickness on growth rate ratio of  $\text{SiO}_2$  on thermal oxide and on nitride. The deposition of high ozone  $\text{SiO}_2$  was carried out at an ozone concentration of  $120 \text{ gm/m}^3$  and a deposition temperature of  $400^\circ \text{C}$ . The conditions were selected to provide a growth rate of  $500 \text{ \AA/min}$ , regardless of the type of substrate.

Figure 5a is a graph that depicts the results of a study in which the SLO was deposited at an ozone concentration of  $1 \text{ gm/m}^3$ . In the absence of any SLO layer ( $0 \text{ \AA}$  thick SLO layer), the growth rate of  $\text{SiO}_2$  on thermal oxide (■) was about 0.35 of that on silicon, and the growth rate of  $\text{SiO}_2$  on nitride (O) was about 0.75 of that on silicon. A SLO layer  $100 \text{ \AA}$  thick increased the growth rate ratio on thermal oxide to about 0.4 and increased the growth rate ratio slightly on nitride. Increasing the thickness of the SLO layer to  $200 \text{ \AA}$  substantially increased the growth rate ratio on thermal oxide, to about 0.8 of that on silicon, and increased the growth rate ratio to about 0.85 on nitride. Further increases in the thickness of the SLO layer increased the growth rate ratio on both thermal oxide and on nitride, but the magnitudes of the increases

were progressively less as thickness increased. In fact, the growth rate ratios for SiO<sub>2</sub> on thermal oxide and nitride did not increase above those obtained for SLO thicknesses of 400 Å.

Figure 5b is a graph that depicts the results of a study in which the SLO layer was deposited at a concentration of 3 gm/m<sup>3</sup>. Subsequent deposition of SiO<sub>2</sub> on either thermal oxide (■) or nitride (O) are shown. As with Figure 5a, the SiO<sub>2</sub> was deposited at a temperature of 400° C and a deposition rate of 500 Å/min at an ozone concentration of 120 gm/m<sup>3</sup>. As with the SLO layer deposited at 1 gm/m<sup>3</sup>, the growth rate ratio for nitride was consistently greater than the growth rate ratio on thermal oxide. Furthermore, increasing SLO thickness above about 400 Å did not cause further increases in growth rate ratio.

**Example 3: Effect of Deposition Temperature of High-Ozone SiO<sub>2</sub> Film on Surface Sensitivity**

In another series of embodiments, we studied the effects of deposition temperature on growth rate ratio for SiO<sub>2</sub> films. In the previously described embodiments, the high ozone SiO<sub>2</sub> film was deposited at a temperature of 400° C. However, by selecting a different deposition temperature, growth rate ratio can be altered to suit particular needs.

Figure 6 is a graph that depicts the relationship between deposition

temperature (in C°) and growth rate ratio of high ozone SiO<sub>2</sub> on nitride compared to that on silicon (■). At a deposition temperature of 400° C, the growth rate ratio was about 0.77 for an oxide film having a thickness of 5000 Å. However, decreasing the temperature to 350° C increased the growth rate ratio to about 0.87. At an intermediate temperature of 375° C the growth rate ratio was between those for 400° C and 350° C. Increasing the temperature to 500° C caused a slight decrease in growth rate ratio, to about 0.74.

Increasing the deposition temperature to about 600° C decreased GRR on nitride to about 0.7. The reduction in GRR on nitride with increasing temperature is unexpectedly different from the effect of temperature on GRR on thermal oxide (see below), where above a certain temperature, the GRR actually increases with increasing temperature.

Figure 7 is a graph that depicts the relationships between the thickness of a SLO and growth rate ratio on thermal oxide at a variety of different deposition temperatures. In each case, the SLO layer was deposited using an ozone concentration of 1 gm/m<sup>3</sup> and the high ozone SiO<sub>2</sub> layer was deposited using an ozone concentration of 120 gm/m<sup>3</sup>. At a deposition temperature of 400° C (■), a SLO layer having a thickness of 100 Å resulted in a growth rate ratio of about 0.4. Increasing the thickness of the SLO layer to either 400 Å or 500 Å increased growth rate ratio to about 0.94. Increasing the temperature to 430° C (O) and 450° C resulted in a progressive shift to lower growth rate

ratios for each SLO layer thickness studied. Surprisingly, increasing the temperature further, to 500° C ( $\Delta$ ), actually increased the growth rate ratio.

## **II. Shallow Trench Isolation Using Super Low Ozone Seed Layers**

5           Using the methods of this invention, it is now possible to manufacture semiconductor devices using shallow trench isolation (STI) having smaller dimensions than previously available, while maintaining desirable electrical and mechanical properties of the dielectric material filling the trench. According to prior art methods, there was considered to be an irreducible minimum thickness  
10           of a low ozone SiO<sub>2</sub> layer that provided satisfactory growth rates of high ozone SiO<sub>2</sub> on thermal oxide and nitride. Unexpectedly, the SLO methods of this invention permit filling, with high quality SiO<sub>2</sub>, of shallow trenches having narrower dimensions than could be filled using prior art methods.

### **A. Shallow Trench Isolation of Trenches Having Liner Oxide**

          The interface between silicon and CVD deposited SiO<sub>2</sub> can produce interfacial stress that decreases useful lifetimes and can cause failure of electrical insulation between devices. To improve the quality of the interface, a layer of liner oxide can be formed using, for example, thermal oxidation.  
20       Liner oxide can decrease the mechanical stresses between the SiO<sub>2</sub> and the surrounding silicon substrate. However, by providing a liner oxide layer of

thermal oxide, the deposition of CVD SiO<sub>2</sub> can result in some of the problems discussed above, including the formation of voids and rough, uneven surfaces. These problems can decrease the effectiveness of the STI.

By the use of super low ozone films of embodiments of this invention  
5 instead of conventional thermal oxide, shallow trench isolation can be carried out using liner oxide and high-quality SiO<sub>2</sub>, without the severe degradation in electrical performance and device lifetimes of prior art methods. Specifically, by the use of SLO methods of this invention, a thin layer of SLO can be deposited in a shallow trench and have sufficient room left in the trench for  
10 deposition of high-quality, high ozone SiO<sub>2</sub>. Thus, for example, a trench having a width of 0.18 μm or less can be adequately filled with both an adequate layer of SLO and high ozone material.

#### **Example 4: Super Low Ozone Liner Oxide**

15 Figure 8 depicts a shallow trench after filling with super low ozone SiO<sub>2</sub> according to an embodiment of this invention. Device **800** is comprised of a silicon substrate **104** having a shallow trench inscribed therein, having a width of 0.15 μm (1500 Å). A layer of liner oxide **106** is formed in the trench and on the surface of wafer **800**. Subsequently, a thin SLO layer **112a** is deposited  
20 using a concentration of ozone selected to form a SLO layer having a thickness of about 200 Å. Thus, the total thickness of the SLO layer **112a** is 2 x 200 Å,

or 400 Å. This leaves 1500 Å - 400 Å (1100 Å) available for high ozone SiO<sub>2</sub> to be deposited within the trench. Subsequently, the remainder of the trench is filled with high ozone SiO<sub>2</sub> layer 116. By filling the trench with high quality SiO<sub>2</sub>, the electrical performance and integrity of the STI can be increased.

5           Using the methods described above, SLO layers can be deposited having thicknesses of about 100 Å, which can be suitable for filling trenches having widths in the range of about 300 Å to about 3500 Å, or greater. In other embodiments, the width of the trench can be in the range of about 1000 Å to about 0.25 μm (2500 Å), and in other embodiments, in the range of about 1800  
10   Å. Thus, by using this SLO layers, one can provide STI having dimensions of 0.15 μm or less for manufacture of future integrated circuits.

#### **B.     Shallow Trench Isolation of Semiconductor Devices Having Nitride Layers**

15           In other embodiments of this invention, the SLO layers can be manufactured upon wafers having nitride layers. Nitride layers exhibit decreased SiO<sub>2</sub> growth rate compared to silicon (Si). Moreover, conditions of deposition can be selected wherein the ratio of SiO<sub>2</sub> deposition on nitride is similar to the rate of deposition on thermal oxide. Therefore, by providing a  
20   nitride layer on an area of a semiconductor device, where decreased deposition of SiO<sub>2</sub> is desired, the growth of SiO<sub>2</sub> be adjusted to more closely reflect the



growth rate of  $\text{SiO}_2$  in the trench.

### **Example 5: Super Low Ozone Layer on Nitride**

Figure 9 depicts an embodiment of this invention in which a semiconductor wafer **900** has a silicon substrate **104**, and a trench inscribed therein having a width of  $0.15\ \mu\text{m}$ . Layers of nitride **118** are depicted on the top surface of wafer **900**. A layer of liner oxide **122** is formed within the trench, and a thin, conformal layer of SLO **112a** is deposited over the liner oxide layer **122** and the nitride layers **118**. The thickness of the SLO layer **112a** is about  $100\ \text{\AA}$ . By providing a SLO layer **112a** having a thickness of  $100\ \text{\AA}$ , there is sufficient room remaining in the trench for the deposition of high quality high ozone  $\text{SiO}_2$  **116**.

In Figure 9, the width of the trench is  $0.15\ \mu\text{m}$  ( $1500\ \text{\AA}$ ), and the SLO layer is  $100\ \text{\AA}$  in thickness. Thus, after deposition of the SLO layer, the amount of room in the trench is  $1500\ \text{\AA} - (2 \times 100\ \text{\AA})$ , or  $1300\ \text{\AA}$ . Moreover, even thinner trenches can be filled using the methods of this invention.

### **III. Methods For Depositing High Ozone Films To Reduce Surface Sensitivity**

In other embodiments of this invention, surface sensitivity of deposition of high ozone  $\text{SiO}_2$  films can be regulated by adjusting the conditions of

deposition, including deposition rate, deposition temperature and thickness of the film. In general, up to a certain point that depends on other deposition conditions, increasing the thickness of the high ozone layer increases the growth rate ratio, regardless of temperature or film deposition rate. Figures 10a - 10c show some of the relationships between deposition variables and surface sensitivity. Additionally, the reduction in surface sensitivity is dependent on the time between the deposition of the low ozone film and the subsequently deposited high ozone film.

**A. Effects of Film Thickness, Deposition Temperature and Deposition Rate on Surface Sensitivity**

In general, for each deposition rate and temperature, surface sensitivity, as reflected in growth rate ratio, increased as the film thickness increased up to a point. In certain embodiments of this invention, that point can be about 3000 Å. Thus, for thicker films, there can be less dependency of GRR on film thickness. Also, higher deposition rates decrease GRR.

**Example 6: Effect of Film Growth Rate on Surface Sensitivity**

Figure 10a is a graph that depicts the results of experiments in which the growth rate of SiO<sub>2</sub> film made with an ozone concentration of 120 gm/m<sup>3</sup> was deposited on wafers having portions of bare silicon, and other portions of

nitride. The growth rate ratio is expressed as the growth rate in Å/min on nitride divided by the growth rate in Å/min on silicon. In this Figure, the growth rate ratios were determined for films deposited at 300 Å/min (\*), 500 Å/min (▲) and 1000 Å/min (Δ) at a deposition temperature of 400° C. The data is plotted with the thickness of the SiO<sub>2</sub> layer on the horizontal axis, and the growth rate ratio (GRR) on the vertical axis.

At the onset of deposition, the GRR decreased for each deposition rate until a minimum GRR was reached. For the highest deposition rate (1000 Å/min) the minimum GRR was about 0.4 at a film thickness of about 800 Å to 1100 Å. For a deposition rate of 500 Å/min, the GRR minimum occurred at a film thickness of between about 500 Å and about 1200 Å, and for the lowest deposition rate (300 Å/min), the minimum GRR of about 0.4 occurred at a film thickness of less than 500 Å. In each case, after the minimum GRR was reached, the GRR increased as the film thickness increased. The increase in GRR was the lowest for the highest deposition rate (1000 Å/min), and was the highest for the lowest deposition rate (300 Å/min). For deposition rates of 300 Å/min and 500 Å/min., the GRR did not increase substantially for films having thicknesses of above about 3000 Å. However, the film deposited at the highest deposition rate (1000 Å/min) showed an increase in GRR at a film thickness of greater than about 6000 Å. However, the GRR for the films deposited at 1000 Å/min remained below the GRRs for either the films deposited at either 300

Å/min or 500 Å/min. There was little difference between GRR for the films deposited at 300 Å/min and 500 Å/min.

#### **Example 7: Effect of Film Deposition Temperature on Surface Sensitivity**

Figure 10b is a graph that depicts the results of experiments similar to those described above for Figure 10a of Example 6, except that the independent variable studied was deposition temperature. SiO<sub>2</sub> films were made with an ozone concentration of 120 gm/m<sup>3</sup> and were deposited on wafers having portions of bare silicon, and other portions of nitride. The growth rate ratio, GRR, is expressed as the growth rate in Å/min on nitride divided by the growth rate in Å/min on silicon. In Figure 10b, the deposition temperature was 350° C. Films were deposited at deposition rates of 300 Å/min (+), 500 Å/min (■) or 1000 Å/min (□). In this series of experiments, as film thickness increased, GRR increased. However, at 350° C, the minimum GRR was observed at somewhat lower film thicknesses than the minima observed at 400° C. Unlike the films deposited at 400° C (Figure 10a), the graphs of GRR versus SiO<sub>2</sub> thickness of films deposited at 350° C appeared to parallel each other, with little difference in GRR observed regardless of the deposition rate.

Figure 10c is a graph that depicts some the results presented in Figures 10a and 10b for deposition rates of 500 Å/min and 1000 Å/min at deposition

temperatures of 350° C and 400° C. The data obtained at a deposition temperature of 400° C is depicted with solid lines. The GRR was lower for films deposited at the higher temperature (400° C) and the higher deposition rate (1000 Å/min;  $\Delta$ ) than films deposited at lower temperatures and deposition rates. Decreasing the deposition temperature to 350° C for a deposition rate of 1000 Å/min ( $\square$ ) increased GRR to values similar to those observed for lower deposition rates (Figures 10a and 10b). A similar effect of temperature was observed at a deposition rate of 500 Å/min. (dashed lines). Decreasing the deposition temperature from 400° C ( $\blacktriangle$ ) to 350 °C ( $\blacksquare$ ) increased GRR to values similar to those observed for 400° C ( $\square$ ).

#### **B. Effect of Post-Low Ozone Film Deposition Time on Surface Sensitivity**

After the deposition of a layer of low ozone film of this invention, we unexpectedly observed that if there was a delay before the deposition of a high-ozone film, the beneficial effects of the low-ozone film began to decrease in efficacy. If the low ozone layer remains exposed to  $O_2/O_3/N_2$  at an elevated temperature (e.g., 400° C), within about 30 minutes, the effect of the low ozone layer on surface sensitivity decreases, such that the subsequently deposited high ozone layer exhibits increased surface sensitivity. The effect is more pronounced if the delay is longer than 30 minutes. Therefore it can be

desirable to apply a high ozone layer soon after deposition of the low ozone layer.

An alternative solution is to provide a cap layer of high ozone film. This cap layer can be relatively thin and need not necessarily provide complete gap filling. Rather, if desired, one can delay the final gap filling so long as a cap layer is provided.

In another embodiment of the invention, one can manufacture a graded film, wherein the initial deposition is carried out using a low ozone concentration and then continuously increasing the ozone concentration as the SiO<sub>2</sub> layer is deposited. The gradient of the ozone film can be adjusted to achieve any desired film composition.

#### IV. Use of Seed Layers To Decrease Surface Sensitivity of High-Ozone SiO<sub>2</sub> Deposition at Different Temperatures

By combining the findings above, using the methods of this invention, surface sensitivity can be adjusted and maintained at a desirable level, regardless of the deposition temperatures used.

#### Example 8: Seed Layers of SiO<sub>2</sub> to Decrease Surface Sensitivity

Figure 11 is a graph that depicts the results of studies designed to determine the effects of SLO seed layers 400 Å thick on the deposition of high

ozone  $\text{SiO}_2$  films at different temperatures, . The growth rate ratio (GRR) expressed as the ratio of growth on thermal oxide to growth on silicon is shown as a function of deposition temperature. The high ozone film of non-doped silicate glass (NSG) was formed using a concentration of ozone of  $120 \text{ gm/m}^3$ ,  
5 and the deposition rate of the high ozone film was  $500 \text{ \AA/min}$ .

In the absence of a SLO seed layer (■), and at a deposition temperature of  $400^\circ \text{ C}$ , the observed GRR was about 0.6. Increasing the temperature decreased GRR to a minimum of about 0.35 at a temperature of about  $430^\circ \text{ C}$ . Further increasing the deposition temperature increased GRR, so that at a  
10 temperature of  $500^\circ \text{ C}$ , the GRR was slightly greater than the GRR observed at  $400^\circ \text{ C}$ .

Other wafers had a  $400 \text{ \AA}$  thick layer of SLO film deposited using an ozone concentration of  $1 \text{ gm/m}^3$  before deposition of high ozone film (O). At a deposition temperature of  $400^\circ \text{ C}$ , GRR was greater than about 0.9.  
15 Increasing deposition temperature of the high ozone film decreased GRR only slightly. At a deposition temperature of about  $450^\circ \text{ C}$ , the GRR was about 0.85, and at a temperature of  $500^\circ \text{ C}$ , the GRR increased to about 0.88.

Therefore, in situations in which a high growth rate of high ozone film is desirable, the addition of a SLO layer can increase growth rate ratio, and  
20 thereby can improve the deposition of  $\text{SiO}_2$  films.

## V. Deposition of Planar Silicon Dioxide Layers On Different Types of Surfaces

By selecting deposition variables described above, a manufacturer can form silicon dioxide layers having improved planarity compared to prior methods, without extensive use of chemical mechanical polishing or alternative planarization techniques. Improved planarity can be accomplished even on wafers having different types of semiconductor materials near to one another.

### A. Equalizing Growth Rate Ratio for Oxide and Nitride

Semiconductor devices can be made having several different types of surfaces on them. Typically, a semiconductor wafer can have bare silicon, thermal or other oxide, and nitride layers. The presence of several different types of materials can cause problems of planarity with the formation of high ozone  $\text{SiO}_2$  films. By way of example, as depicted in Figures 12a - 12c, a semiconductor wafer **1200** can have a silicon substrate **104**, a layer of oxide **106** and a layer of nitride **118**. According to prior art methods for the CVD deposition of  $\text{SiO}_2$  using TEOS/ $\text{O}_3$ , the deposition of a relatively thin layer of high ozone  $\text{SiO}_2$  (Figure 13a) can result in the formation of a film **116** that does not adequately fill the spaces between the oxide **106** and the nitride **118**. The result can be an uneven film **116** having poor planarity.

Attempting to remedy this situation by depositing a thicker layer of high



ozone  $\text{SiO}_2$  (Figure 12b) can result in additional problems. Differential deposition rates of  $\text{SiO}_2$  on silicon compared to that on nitride (see Figures 3, 5a and 5b) can permit the deposition of a film that is relatively even over the silicon substrate **104** and the nitride layer **118**. However, because the growth rate of high ozone  $\text{SiO}_2$  on oxide **106** can be lower than the growth rates on either silicon or nitride (see Figures 3, 5a and 5b), the layer **116** of high ozone  $\text{SiO}_2$  is thinner over oxide layer **106** than over nitride layer **118** or silicon substrate **104**. Thus, the surface of  $\text{SiO}_2$  layer **116** is non-planar.

Further attempts to thicken the  $\text{SiO}_2$  layer **116** over oxide layer **106** can result in further non-planarity of the insulating layer. Figure 12c depicts a semiconductor wafer **1200** of the prior art as in Figures 12a and 12b after having a thicker layer **116** of high ozone  $\text{SiO}_2$  deposited thereon. Although the thickness of layer **116** on oxide layer **106** is greater than for Figure 12b, the additional deposition of  $\text{SiO}_2$  on silicon substrate **104** and nitride layer **118** can result in layers of  $\text{SiO}_2$  that are too thick, especially over the areas of silicon **104**. Therefore, prior art methods for differential deposition can have limited applicability to semiconductor wafers having different types of semiconductor materials near to one another.

In another series of embodiments of this invention, the difference between growth rate ratios for oxide and nitride on silicon can be reduced. According to the methods of this invention, it can be desirable to take

advantage of the differential surface sensitivity of nitride compared to oxide. By using SLO layers of this invention, the difference in  $\text{SiO}_2$  growth rates on thermal oxide and nitride can be reduced, making deposition rates similar over both surfaces.

5           Figure 13 depicts a semiconductor wafer of this invention **1300** having silicon substrate **104**, oxide layer **106**, and nitride layer **118**. By referring to Figures 3, 5a, 5b, or Table 2, a manufacturer can choose a SLO layer made with a selected ozone concentration at a selected thickness. For example, referring to Figure 3, selecting an ozone concentration of about  $1 \text{ gm/m}^3$  or less  
10       can provide growth rate ratios for  $\text{SiO}_2$  on thermal oxide and on nitride of about 0.93. By selecting a SLO layer having a thickness of about  $400 \text{ \AA}$  (Figure 5a) and by depositing SLO layer **112a** over the silicon substrate **104**, oxide layer **106** and nitride layer **118**, the subsequent high ozone  $\text{SiO}_2$  layer **116** can be formed more evenly over nitride layer **118** and oxide layer **106**. By increasing  
15       the growth rate of  $\text{SiO}_2$  over oxide compared to that over nitride, the overall planarity of the film **116** can be improved without the need for excessive additional planarization.

### **B. Increasing Surface Sensitivity to Provide Improved Planarity**

In yet other embodiments of this invention, a manufacturer can take advantage of the phenomenon observed and presented in Figures 6 and 11 wherein increasing deposition temperature can provide improved planarity of silicon dioxide layers. By way of example only, after the deposition of a low temperature SLO layer under conditions selected to provide relatively equal deposition rates of  $\text{SiO}_2$  on nitride and oxide (e.g., ozone concentration of 1 gm/m<sup>3</sup> or lower, SLO layer thickness, about 400 Å, SLO deposition temperature, 350° C) , a subsequent high ozone film can be formed at a higher temperature. As shown in Figure 6, increasing the deposition temperature of a high ozone film on nitride from 350° C to 500° C can decrease the growth rate ratio on nitride. In contrast, on thermal oxide, increasing the temperature to 500° C can increase growth rate ratio. Thus, to promote more rapid growth on thermal oxide compared to nitride, it can be desirable to use higher deposition temperatures. Because the growth rate ratios for nitride and oxide can be made more equal by a SLO layer, increasing the temperature of deposition of the high ozone layer, the growth rate ratio for both  $\text{SiO}_2$  and nitride is reduced, compared to silicon, thereby providing more rapid growth of  $\text{SiO}_2$  over the silicon substrate than over either the SLO-covered oxide or SLO-covered nitride layers. Therefore, using high temperature deposition, a substantially

planar surface can be manufactured using a thinner high ozone  $\text{SiO}_2$  layer, compared to the deposition of high ozone films at lower temperatures (e.g.,  $400^\circ\text{C}$ ).

5           **Example 9: Planar  $\text{SiO}_2$  Layers Using High Temperatures**

Figure 14 illustrates an embodiment of the invention using different deposition temperatures for the SLO layer and the high ozone layer. Semiconductor wafer **1400** comprises a silicon substrate **104**, an oxide layer **106** and a nitride layer **118**. On the surface of these materials, a SLO layer **112a** is deposited at a temperature of  $350^\circ\text{C}$  using an ozone concentration of about  $1\text{ gm/m}^3$  or less, and having a thickness of about  $400\text{ \AA}$ . According to Figures 5a and 10c, these conditions can produce a SLO film having relatively equal growth rate ratios for  $\text{SiO}_2$  on nitride and oxide. Subsequently, deposition of high ozone film **116a** at a temperature of about  $500^\circ\text{C}$  can deposit more  $\text{SiO}_2$  over silicon substrate **104** than over either oxide layer **106** or nitride layer **118**. As a result, the finished  $\text{SiO}_2$  film **116a** can be planar and can be thinner than the corresponding, lower temperature film of Figure 13.

10

15

### C. Altering Surface Sensitivity by Altering Deposition Temperature and Deposition Rate

In other embodiments of this invention one can alter growth rate by selecting the temperature of deposition and the deposition rate of the silicon dioxide film. To illustrate this aspect of the invention, one can first grow a layer of high ozone TEOS/ozone oxide at a low deposition rate at a high ozone concentration and a low temperature, such as about 350° C to about 400° C. These deposition conditions can provide a layer of oxide with a high growth rate ratio, or GRR. However, the planarity of the layer grown under these conditions may not be suitable. Therefore, to achieve improved planarity, one can subsequently grow additional oxide film under conditions that reduce GRR. Reducing GRR decreases the growth rate on the nitride or thermal oxide portions of the wafer compared to the silicon portions of the wafer. To accomplish this aim, one can increase the deposition rate at the same temperature, or one can maintain the deposition rate but increase the temperature, both of which can reduce GRR. This strategy can be illustrated by reviewing the data of Figure 10a.

As seen in Figure 10a, by growing a film at a high GRR at 300 Å/min, a desired film having a thickness of 5000 Å would take a long time to grow, and would not be very planar. Increasing deposition rate to 1000 Å/min decreases GRR, thereby permitting growth on silicon to proceed relatively more rapidly

than on nitride or thermal oxide, and therefore increasing planarity. This also decreases the time needed to grow the film. More generally, one can grow a film at a deposition rate 1 at temperature 1 and then choose deposition rate 2 at temperature 2 to achieve alterations in GRR to suit the particular application.

5

**D. Increasing Ozone Concentration to Provide Improved Planarity**

In other embodiments of this invention, the planarity of  $\text{SiO}_2$  on mixed  
10 semiconductor materials can be improved by the use of higher ozone concentrations during the deposition of  $\text{SiO}_2$ , known herein as super high ozone (“SHO”). We have unexpectedly found that increasing the ozone concentration, to values above those of the prior art, increases the surface sensitivity of  $\text{SiO}_2$  deposition on nitride and thermal oxide compared to silicon.  
15 This method of increasing surface sensitivity (the “SHO” method) can be useful in situations in which it is desired to deposit  $\text{SiO}_2$  on silicon at a greater degree than on nitride or thermal oxide. For example, the ozone concentration for SHO deposition can be in the range of about  $120 \text{ gm/m}^3$  to about  $320 \text{ gm/m}^3$ . In alternative embodiments, the ozone concentration can be in the range of  
20 about 160 to about  $250 \text{ gm/m}^3$ , and in other embodiments, about  $180 \text{ gm/m}^3$ . The SHO method can be used either alone or in combination with increasing the temperature of the high ozone film.

**Example 10: Planar SiO<sub>2</sub> Layers Using High Ozone Concentration**

Figures 15a - 15c depict a method for SiO<sub>2</sub> deposition according to this invention. In Figure 15a, a silicon wafer **1500** has a silicon substrate **104** and trench **108** with a layer of nitride **118** deposited on the surface of the silicon substrate. Deposition of a high ozone SiO<sub>2</sub> layer using ozone concentration of 120 gm/m<sup>3</sup> according to this invention can result in a planar surface **119** of layer of SiO<sub>2</sub> **116**. However, the thickness “T” of layer **116** is undesirably large.

Figure 15c depicts a method of this invention for SiO<sub>2</sub> deposition to achieve planar SiO<sub>2</sub> layers on a semiconductor device **1500**. Figure 15c depicts the same structure as shown in Figure 15a, but the concentration of ozone during the deposition of the high ozone layer is 250 gm/m<sup>3</sup>, compared to the 120 gm/m<sup>3</sup> ozone concentration as depicted in Figure 15b. The total thickness “t” of the SiO<sub>2</sub> layer necessary to achieve planarity of the surface is smaller than the SiO<sub>2</sub> layer needed to achieve planarity using a lower ozone concentration depicted in Figure 15b.

By combining the effects of SHO and increased deposition temperature, even higher effects of GRR can be achieved. There can be a synergistic effect, wherein the combined effect of increasing deposition temperature and increasing ozone concentration can result in alterations of GRR that are greater than the additive effect of each separately. Based on the results shown in Figures 6 and 11, the effect of temperature alone cannot result in a growth rate

on thermal oxide greater than that on nitride. As shown in Figure 11, the GRR on thermal oxide is generally below 0.7, whereas the minimum GRR on nitride is depicted in Figure 6 to be greater than about 0.7. However, by combining the SHO and increased temperature, growth rate on thermal oxide can be  
5 greater than that on nitride. This synergism is completely unexpected.

**Example 11: Shallow Trenches Filled with SiO<sub>2</sub> Without Weak Seams**

Figures 16a and 16b are electron micrographs of semiconductor devices  
10 **1600** of this invention having low ozone and high ozone layers (the “super low-high ozone” process). Figure 16a depicts an electron micrograph showing a cross section of a semiconductor wafer having a substrate **104** of silicon, shallow trenches having a width of 0.22 μm, and nitride caps **118** on the topmost portions of the silicon substrate **104**. The trenches have been filled  
15 with a low ozone film and a high ozone film according to methods of this invention, thereby filling the trench with SiO<sub>2</sub> **116**. There are no observable weak seams or voids, and the trench is completely filled. The scale bar is 375 nm long.

Figure 16b is an electron micrograph of a semiconductor wafer having  
20 a silicon substrate **104**, a shallow trench, and nitride caps **118** on the topmost portions of the silicon substrate **104**. In this embodiment, a layer of liner oxide



122 was provided prior to the deposition of the low ozone TEOS film and the subsequently deposited high ozone TEOS film. As with Figure 16a above, the trench is completely filled with SiO<sub>2</sub> 116, and no weak seams or voids are visible. The scale bar is 300 nm long.

5

**Example 12: Improved Planarity of SiO<sub>2</sub> Films Using Super High Ozone**

In another embodiment of this invention, one can form a shallow trench and fill it with super high ozone SiO<sub>2</sub>. Figures 17 a - 17 b depict this type of embodiment 1700. In Figure 17a, a silicon wafer 1700 is formed having a silicon substrate 104, nitride caps 118 and shallow trenches 108. In Figure 17b, a wafer 1700 as depicted in Figure 17a, has been filled with a high ozone SiO<sub>2</sub> film 117 of this invention. The top surface 120 of film 117 is planar, reflecting the higher growth rate of the high ozone SiO<sub>2</sub> film over silicon substrate 104 compared to the growth rate on the nitride caps 118.

This embodiment was found to effectively fill shallow trenches and to provide a substantially planar surface. We measured the gap filling of trenches 0.2 μm in width on silicon (1:0:0) wafers without a liner oxide layer. The deposition temperature was 500° C, O<sub>2</sub> flow rate was 7.5 standard liters per minute (slm), the O<sub>3</sub> concentration was 120 gm/m<sup>3</sup>, the N<sub>2</sub> flow rate was 18 slm, the film deposition rate, as targeted to blank wafers, was 500 Å/min, and

the film thickness, as targeted to blank wafers, was 1200 Å.

Figure 18 depicts a scanning electron micrograph of a cross section of a silicon wafer **1800** having shallow trenches, nitride caps **118** and a layer of SiO<sub>2</sub> **117** deposited as described above. As with Figure 16, the shallow  
5 trenches are filled with SiO<sub>2</sub> **117** having no weak seams. Further, the thickness of the SiO<sub>2</sub> layer over the silicon substrate **104** (i.e., in the trenches) is much thicker than the thickness of the SiO<sub>2</sub> layer over the nitride caps **118**. Thus, the growth rate ratio of SiO<sub>2</sub> on Si vs the rate on nitride was observed to be about 0.18. Moreover, the top surface **120** is substantially planar.

10 By permitting the film to grow thicker, the top surface will be even more even and planar than observed in Figure 18.

By selecting the ozone concentration used for SLO deposition, the deposition temperature and the thickness of the SLO layer, the type of substrate, and the conditions of deposition of high ozone films, the methods of  
15 this invention can provide a semiconductor manufacturer with a variety of combinations of SLO and SHO layers suited for a variety of particular applications. By selecting these variables, semiconductor devices can be made that have reduced device dimensions, improved electrical performance, and increased device reliability.

20 Unless otherwise specifically incorporated by reference, each and every reference cited is herein incorporated fully by reference.

Although the invention is described by reference to specific embodiments, the invention is not limited to the specifically disclosed embodiments. Workers of skill in the art can modify the methods of this invention to arrive at numerous other embodiments through no more than  
5 routine experimentation, and each of these embodiments is also considered to be part of this invention.

### **INDUSTRIAL APPLICABILITY**

Methods are provided for the manufacture of thin layers of  $\text{SiO}_2$  made  
10 using super low, high, and super high ozone concentrations. The SLO layers can accommodate the manufacture of shallow trench isolation using trenches of smaller width than conventional methods permit. The semiconductor devices made using the methods of this invention can have improved electrical and mechanical properties and increased useful lifetimes.

**We Claim:**

1. A method for manufacturing a thin film of silicon dioxide, comprising the steps of:
  - (a) forming a first layer of silicon dioxide thereon using ozone at a first ozone concentration in the range of about 0.01 gm/m<sup>3</sup> to about 20 gm/m<sup>3</sup>; and
  - (b) forming a second layer of silicon dioxide using ozone at a second ozone concentration higher than said first ozone concentration on said first silicon dioxide layer.
2. A method for manufacturing a thin film of silicon dioxide on a substrate, comprising the steps of:
  - (a) forming a first layer of silicon dioxide having a thickness in the range of about 100 Å to less than about 1000 Å thereon at a first ozone concentration; and
  - (b) forming a second layer of silicon dioxide at a second ozone concentration higher than said first ozone concentration on said first silicon dioxide layer.
3. A method for manufacturing a thin film of silicon dioxide on a substrate, comprising the steps of:

- (a) forming a first layer of silicon dioxide having a thickness in the range of about 100 Å to less than about 1000 Å thereon at an ozone concentration in the range of about 0.01 gm/m<sup>3</sup> to about 20 gm/m<sup>3</sup>; and
- 5 (b) forming a second layer of silicon dioxide at a second ozone concentration higher than said first ozone concentration on said first silicon dioxide layer.
4. A method for manufacturing a shallow trench isolation for a semiconductor device, comprising the steps of:
- 10 (a) providing a silicon substrate having a shallow trench having a width less than about 0.25 micrometers thereon;
- (b) forming within said shallow trench, a first layer of silicon dioxide having a thickness in the range of about 100 Å to less than about 1000 Å thereon at a first ozone concentration; and
- 15 (c) forming within said shallow trench, a second layer of silicon dioxide at a second ozone concentration higher than said first ozone concentration on said first silicon dioxide layer.
- 20 5. The method of claim 4, wherein the shallow trench has a width less than about 0.18 micrometers.

6. The method of claim 4, wherein the shallow trench has a width less than about 0.15 micrometers.
7. The method of claim 1, wherein the ozone concentration used in step  
5 (b) is gradually changed during deposition to the ozone concentration used in step (c).
8. The method of claim 1, wherein said first ozone concentration used in  
step (a) is higher than said second ozone concentration used in step (b).  
10
9. The method of claim 8, wherein the ozone concentration used in step  
(a) is gradually changed during deposition to the ozone concentration  
used in step (b).
- 15 10. A method for manufacturing a semiconductor device, comprising the  
steps of:
  - (a) providing a silicon substrate having at least a layer of silicon and  
a second layer thereon;
  - (b) selecting a condition for deposition of a first silicon dioxide  
20 layer on said layer of silicon and said second layer, said  
condition for deposition being selected from the group

consisting of ozone concentration, deposition temperature, rate of deposition and thickness of said silicon dioxide layer;

(c) depositing a first silicon dioxide layer under deposition conditions of step (b) on said layer of silicon and said second layer; and

(d) depositing a second layer of silicon dioxide at a second ozone concentration higher than said first ozone concentration on said first silicon dioxide layer deposited in step (c).

10 11. The method of claim 10, wherein the temperature used in step (d) is higher than the temperature used in step (c).

12. The method of claim 1, wherein the ozone concentration in step (a) is in the range of about 1 gm/m<sup>3</sup> to about 5 gm/m<sup>3</sup>.

15

13. The method of claim 1, wherein the ozone concentration in step (a) is in the range of about 0.5 gm/m<sup>3</sup> to about 3 gm/m<sup>3</sup>.

14. The method of claim 1, wherein the temperature of deposition of the film deposited in step (a) is in the range of about 300° C to about 800° C.

20

15. The method of claim 1, wherein the temperature of deposition of the film deposited in step (a) is in the range of about 350° C to about 650° C.
- 5 16. The method of claim 1, wherein the temperature of deposition of the film deposited in step (a) is in the range of about 375° C to about 600° C.
- 10 17. The method of claim 1, wherein the thickness of said film formed in step (a) is in the range of about 200 Å to about 700 Å.
- 18 The method of claim 1, wherein the thickness of said film formed in step (a) is in the range of about 300 Å to about 600 Å.
- 15 19. The method of claim 1, wherein the thickness of said film formed in step (a) is in the range of about 400 Å to about 500 Å.
20. A method for manufacturing a thin film of silicon dioxide on a semiconductor wafer, comprising the steps of:
- 20 (a) providing a semiconductor wafer having a layer of nitride formed thereon;



- (b) forming shallow trenches in said wafer;
  - (c) forming a layer of silicon dioxide thereon using ozone at an ozone concentration in the range of about 0.01 gm/m<sup>3</sup> to about 20 gm/m<sup>3</sup>; to form a layer of liner oxide therein; and
  - (d) forming a layer of silicon dioxide on the layer formed in step (c) at an ozone concentration higher than the ozone concentration of step (c).
- 10      21. A method for manufacturing a planar thin film of silicon dioxide on a semiconductor wafer, comprising the steps of:
- (a) providing a semiconductor wafer having a layer of nitride formed thereon;
  - (b) forming at least one shallow trench in said wafer;
  - (c) forming a layer of silicon dioxide in said trench and on said nitride layer at an ozone concentration in the range of about 120 gm/m<sup>3</sup> to about 320 gm/m<sup>3</sup>; and
  - (d) permitting the silicon dioxide layer to grow until a top surface of silicon dioxide over said shallow trench is about planar with a top surface of silicon dioxide over said nitride layer.

22. The method of claim 21, wherein said ozone concentration is about 160 gm/m<sup>3</sup>.
23. The method of claim 1, wherein the thickness of the silicon dioxide layer formed in step (b) is in the range of about 1000 Å to about 6000 Å.
24. A method for manufacturing a semiconductor device, comprising the steps of:
- 10 (a) providing a silicon substrate having at least a layer of silicon and a second layer of material thereon;
- (b) determining the relationships between a condition for deposition of silicon dioxide on said layer of silicon and said second layer of material, said condition being selected from the group
- 15 consisting of ozone concentration, deposition temperature, rate of deposition and thickness of said silicon dioxide layer;
- (c) depositing a first silicon dioxide layer under deposition conditions of step (b) on said layer of silicon and said second layer determined to provide a substantially planar top surface of
- 20 said silicon dioxide layer; and
- (d) depositing a second layer of silicon dioxide so that the top layer

of said silicon dioxide layer is substantially planar over said silicon and said second layer of material.

25. A thin film of  $\text{SiO}_2$  comprising a first layer having a thickness in the  
5 range of about 100 Å to less than about 1000 Å made at a first ozone  
concentration in the range of about 0.01 gm/m<sup>3</sup> and about 20 gm/m<sup>3</sup>  
and a second layer made at a second ozone concentration greater than  
said first ozone concentration.
- 10 26. A thin film of  $\text{SiO}_2$  comprising a first layer made using ozone at a first  
concentration in the range of about 0.01 gm/m<sup>3</sup> and about 20 gm/m<sup>3</sup>  
and a second layer made using ozone at a higher concentration than said  
first ozone concentration.
- 15 27. A graded thin film of  $\text{SiO}_2$  having a first layer made using ozone at a  
first concentration in the range of about 0.01 gm/m<sup>3</sup> to about 20 gm/m<sup>3</sup>  
and subsequent layers made using progressively higher ozone  
concentrations.
- 20 28. The method of claim 24, wherein said second material is selected from  
the group consisting of nitride and thermal oxide.

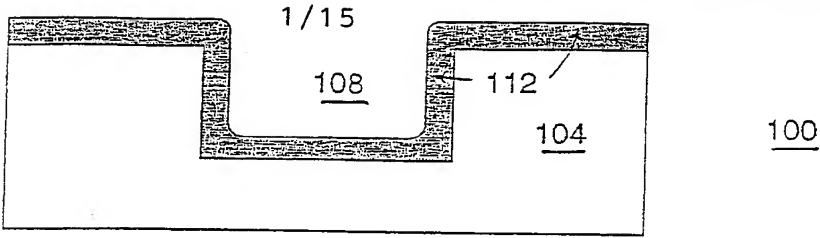


FIGURE 1a Prior Art

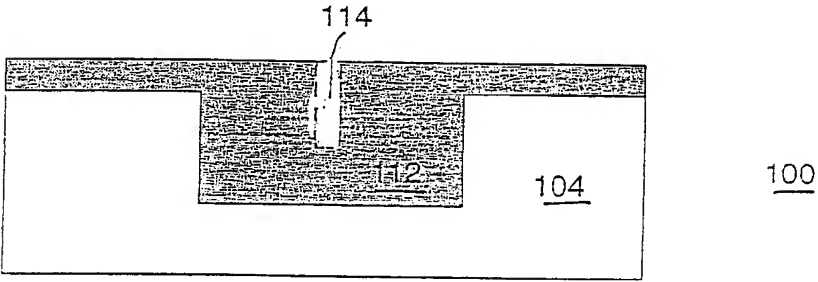


FIGURE 1b Prior Art

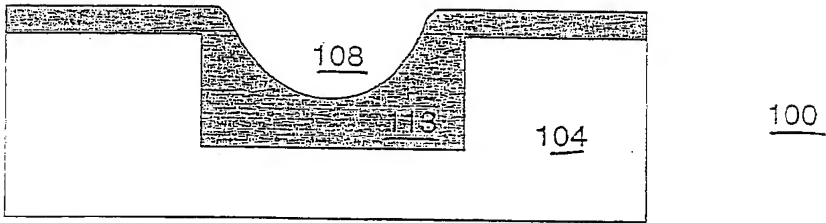


FIGURE 1c Prior Art

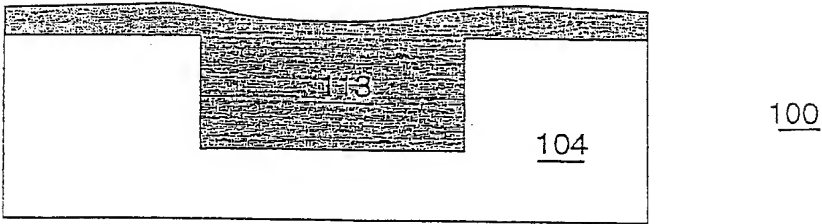
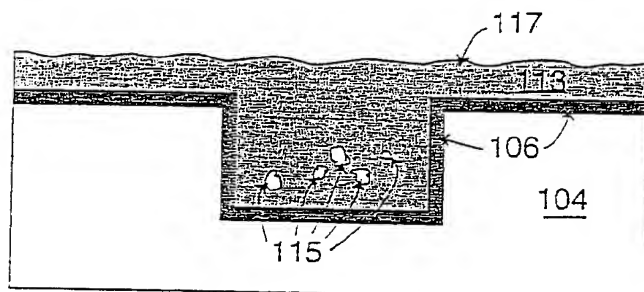
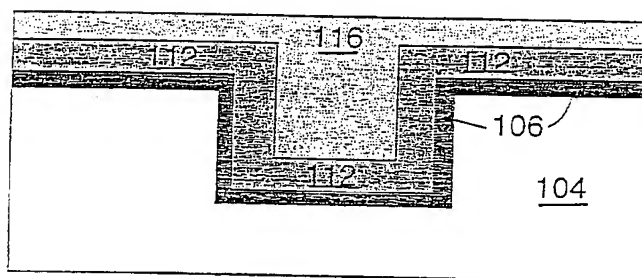


FIGURE 1d Prior Art



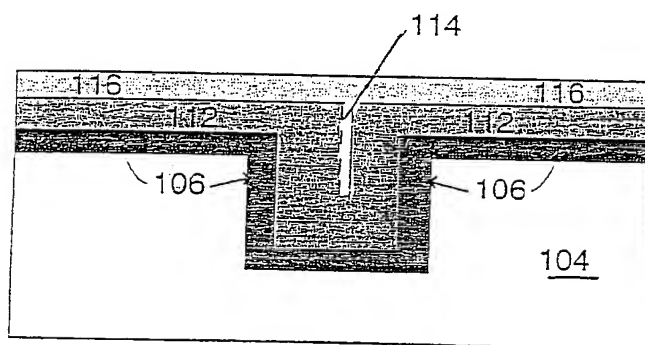
100

FIGURE 1e Prior Art



100

FIGURE 1f Prior Art



100

FIGURE 1g Prior Art

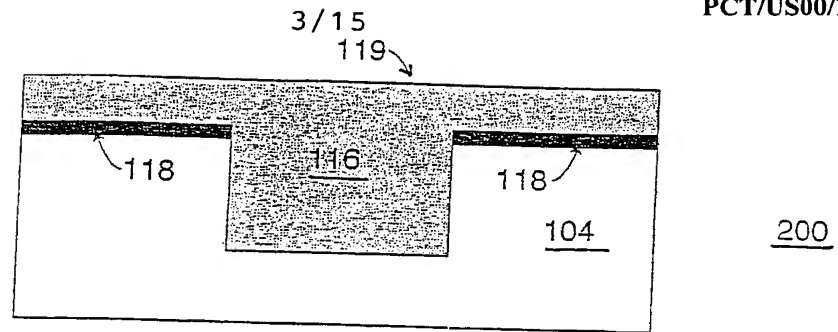


FIGURE 2a Prior Art

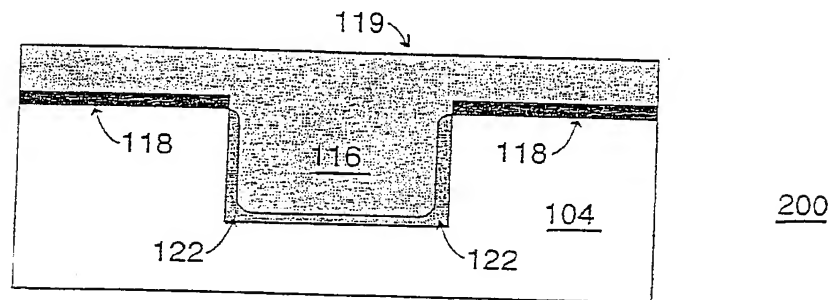


FIGURE 2b Prior Art

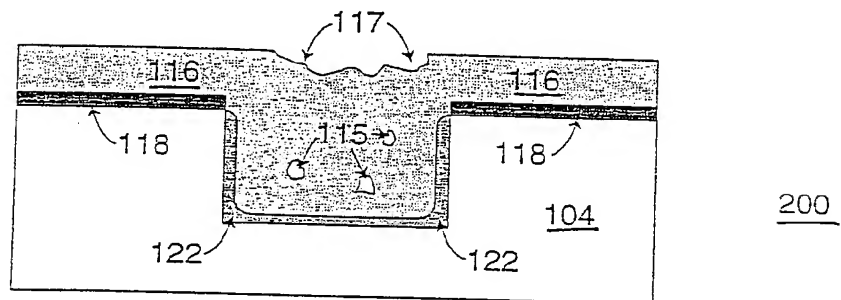


FIGURE 2c Prior Art

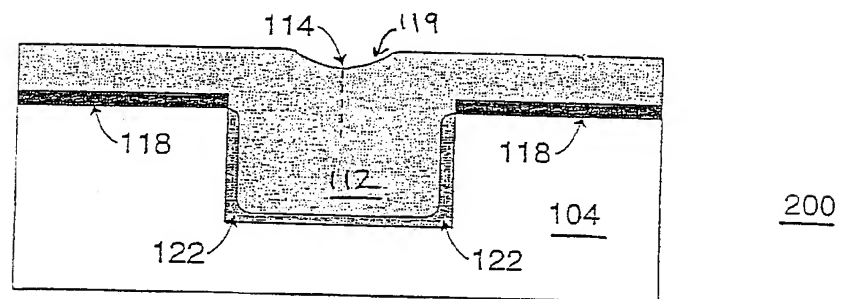


FIGURE 2d Prior Art

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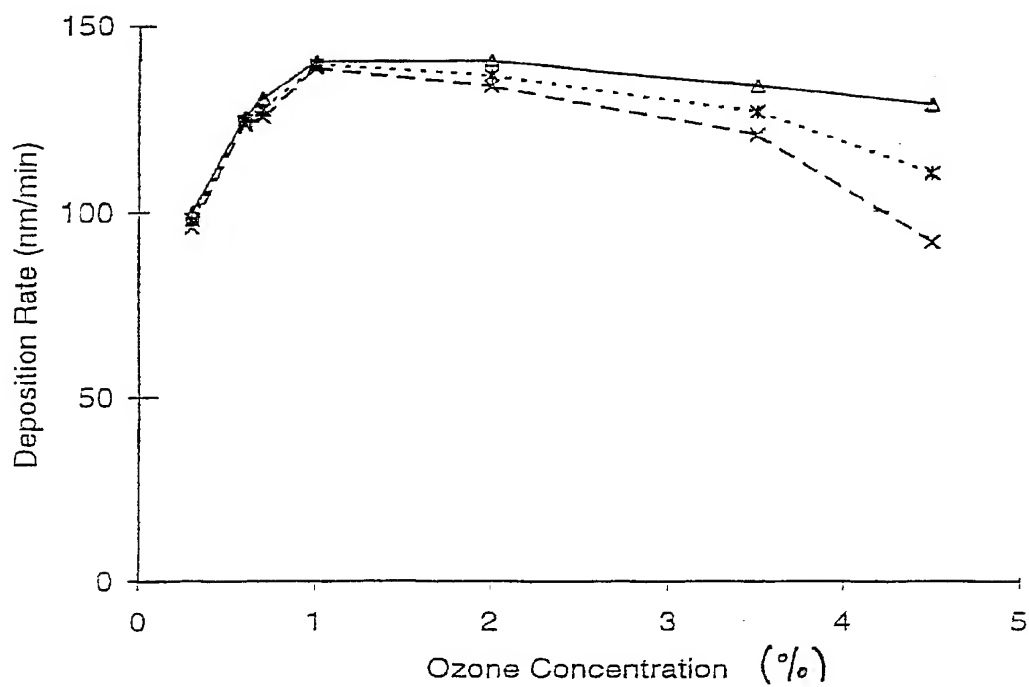


FIGURE 3

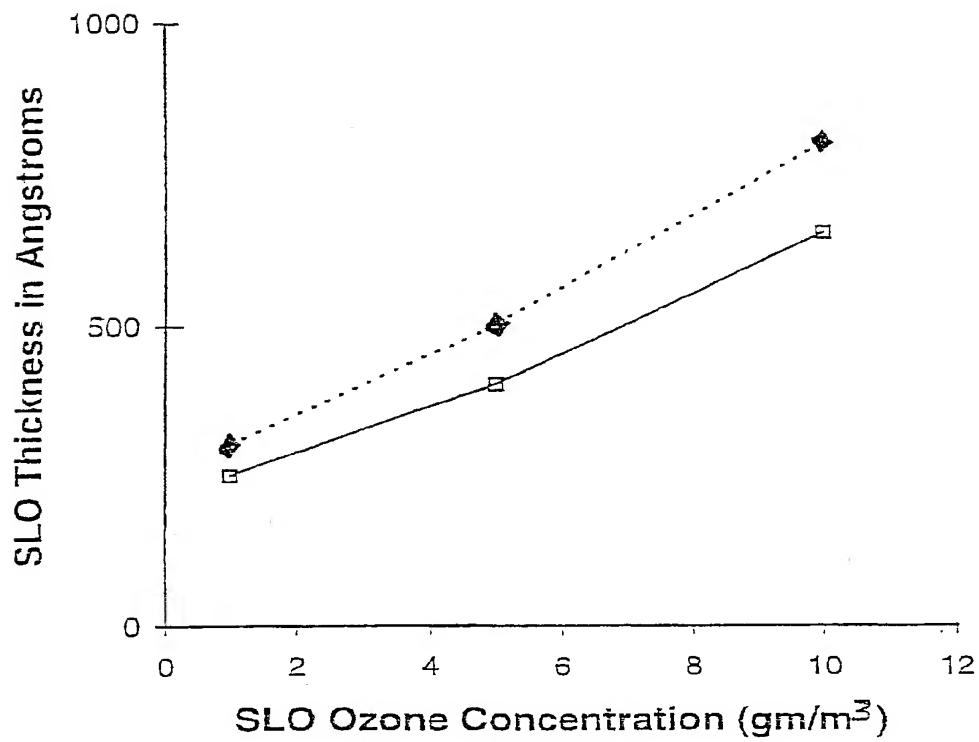


FIGURE 4

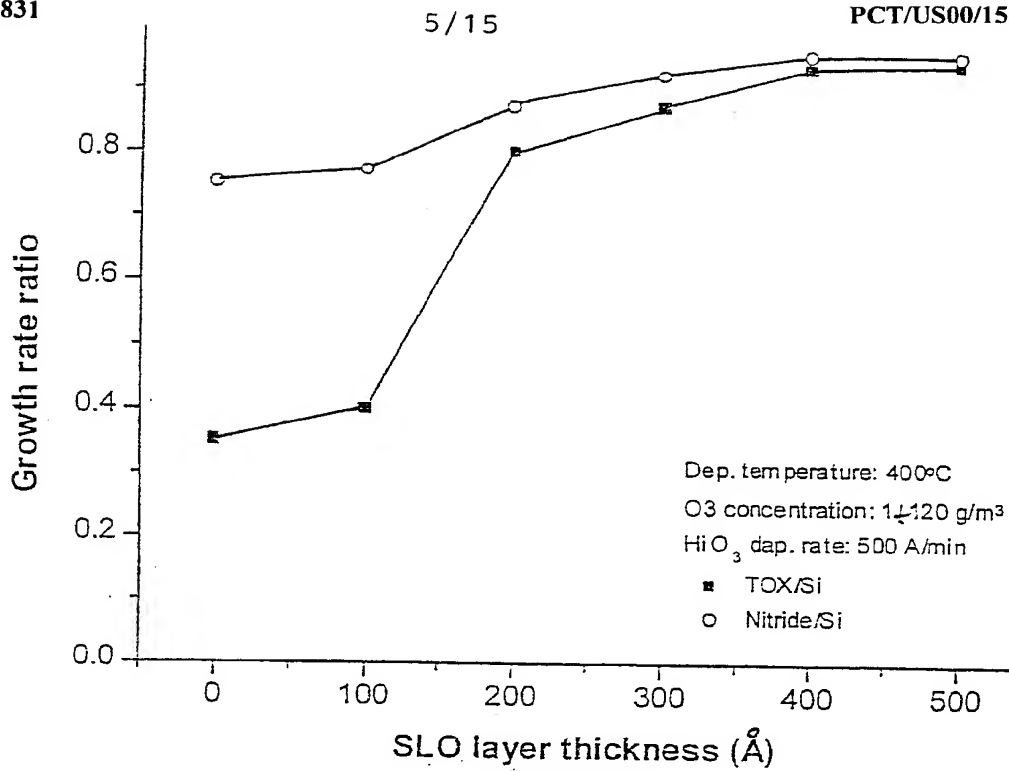


FIGURE 5a

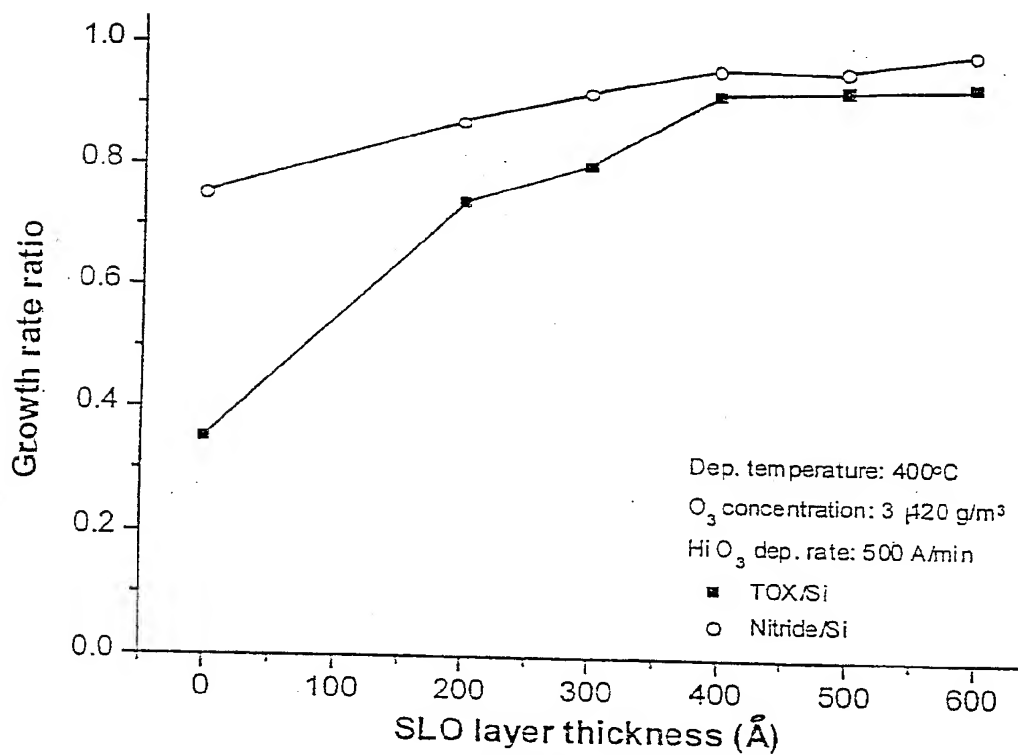


FIGURE 5b



6/15

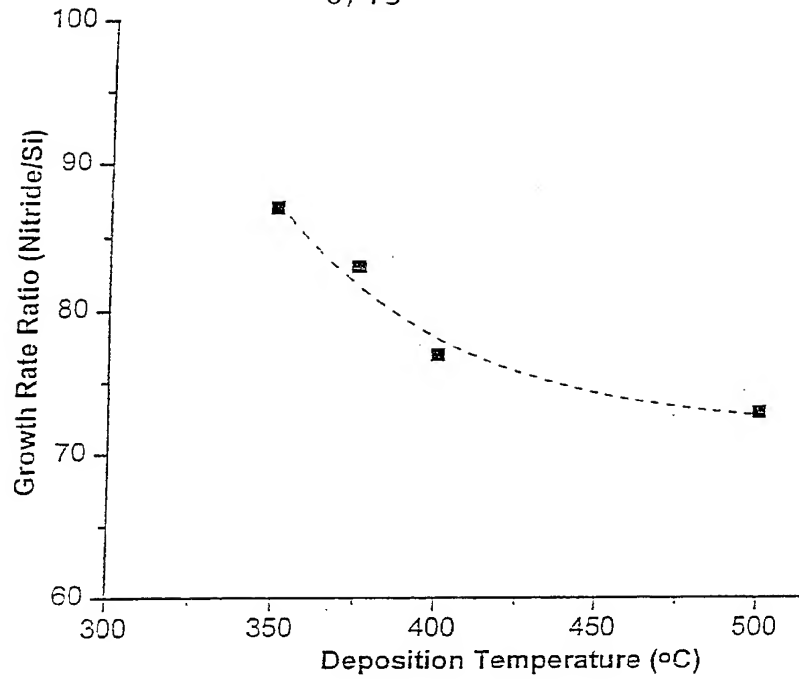


FIGURE 6

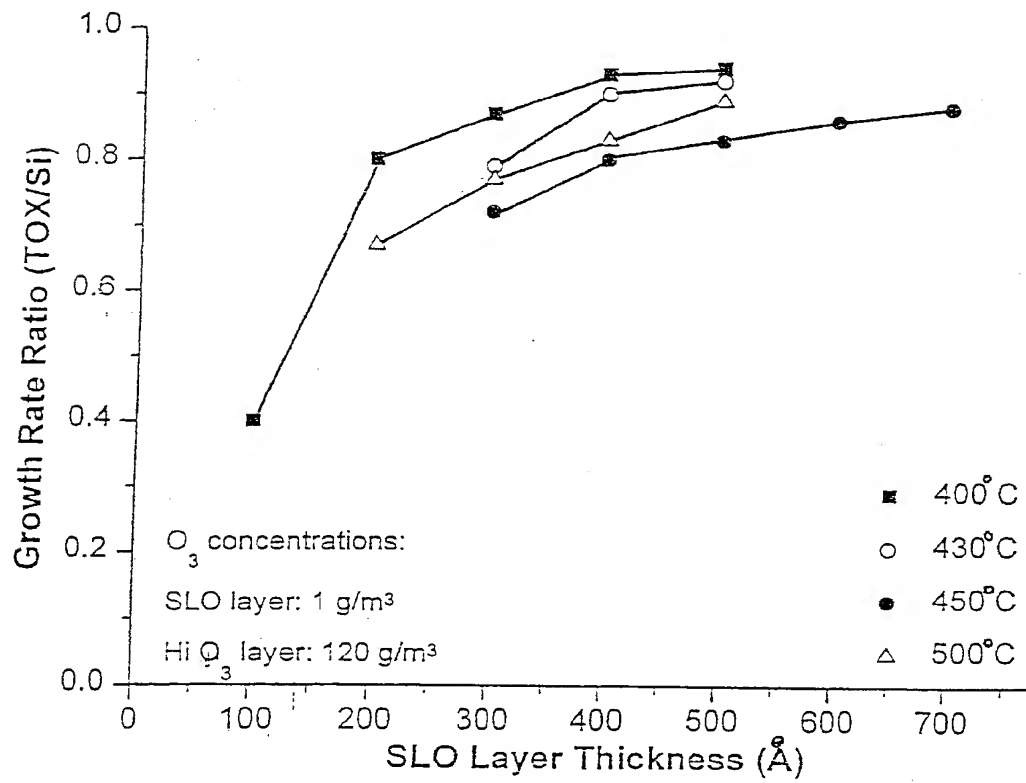
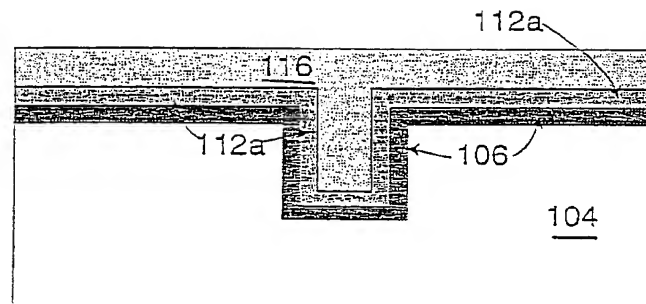
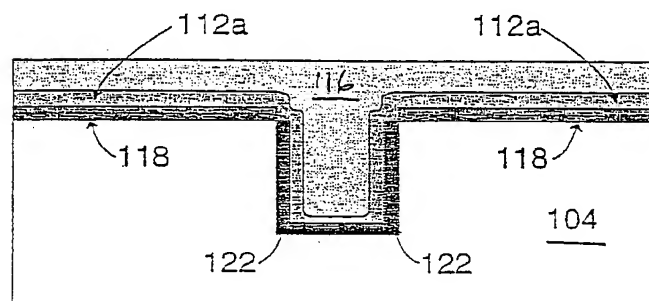


FIGURE 7



800

FIGURE 8



900

FIGURE 9

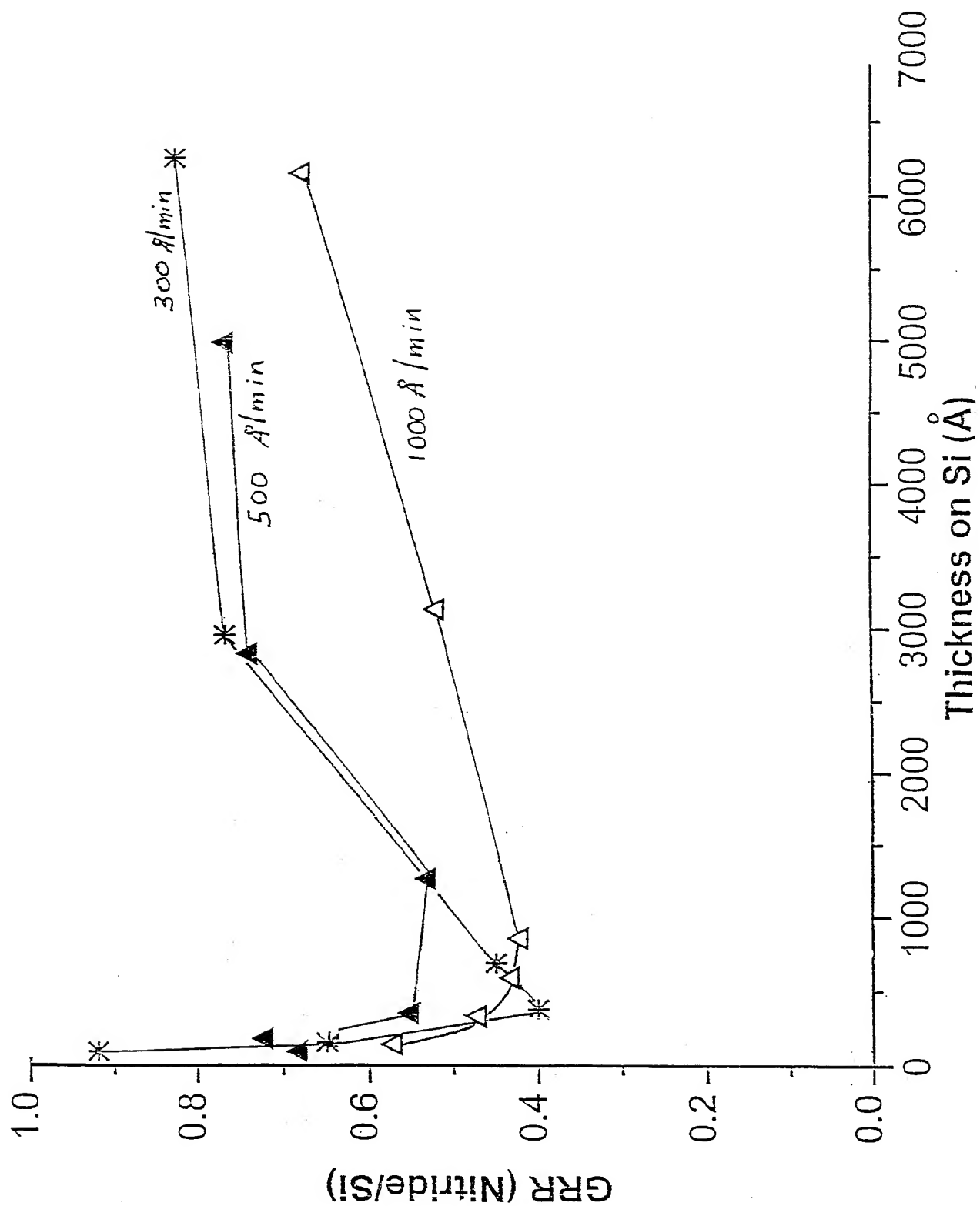


FIGURE 10a

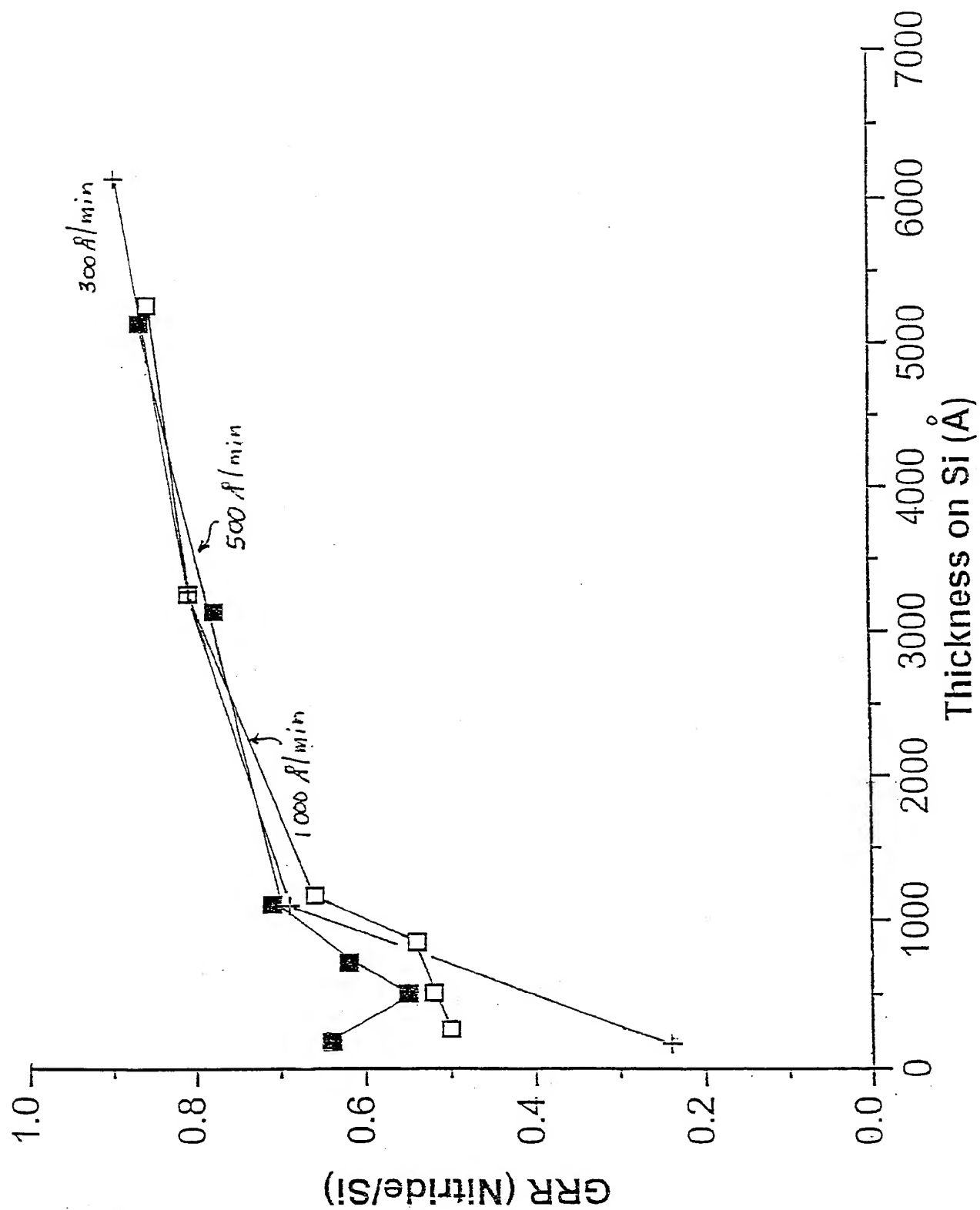


FIGURE 10b

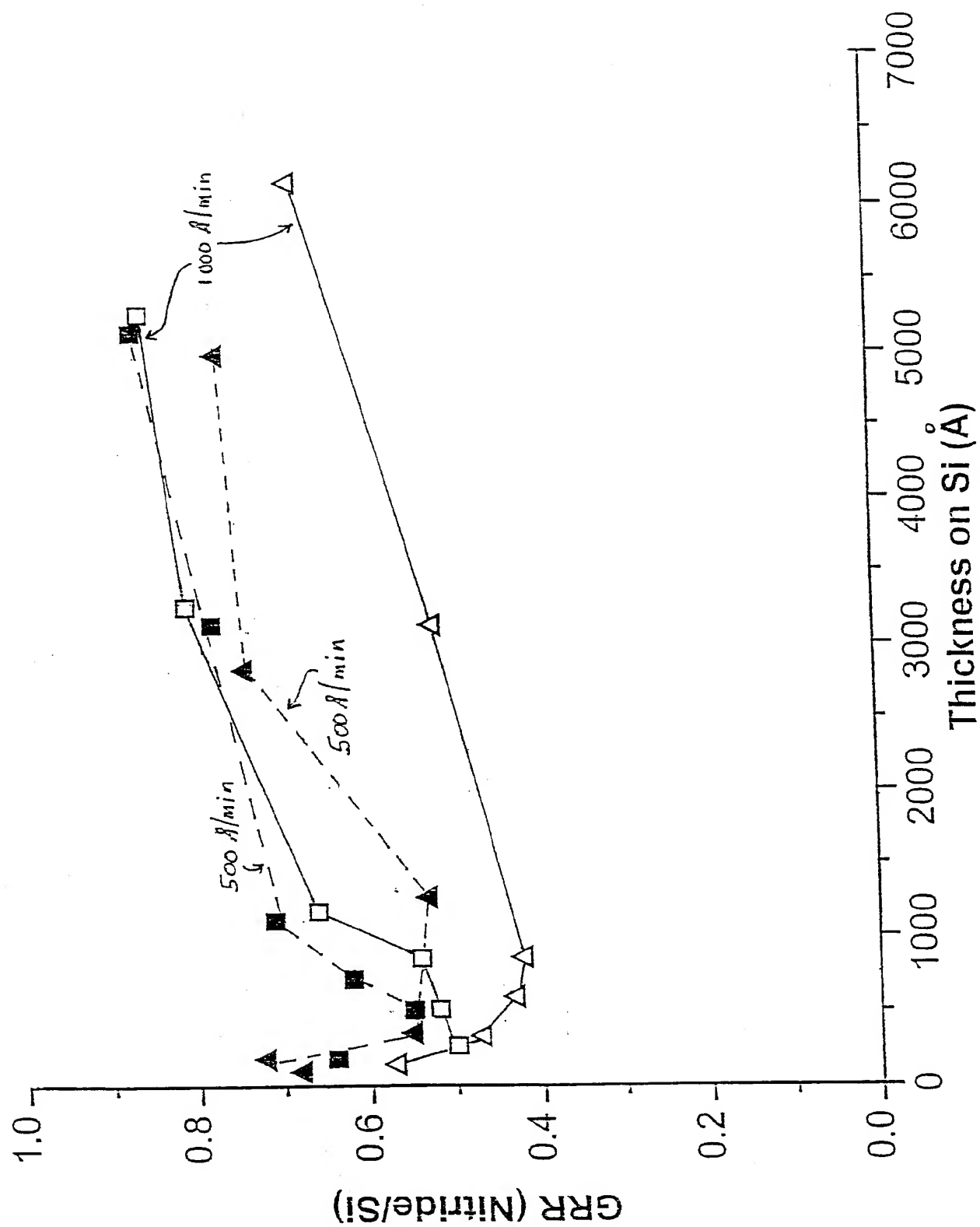


FIGURE 10c

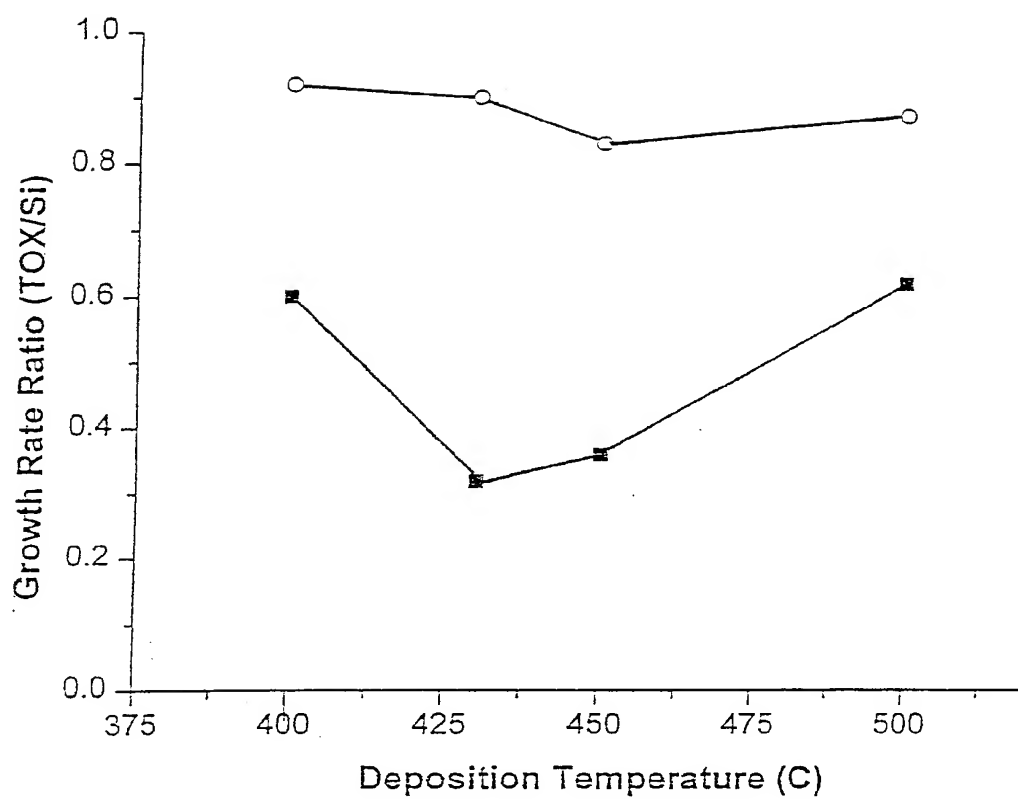
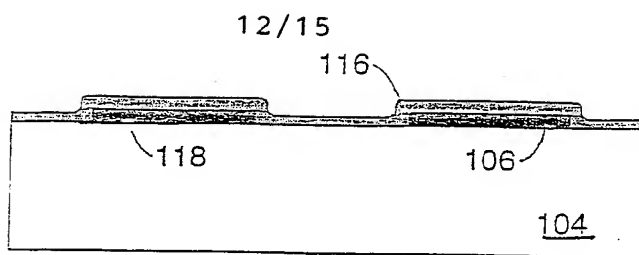
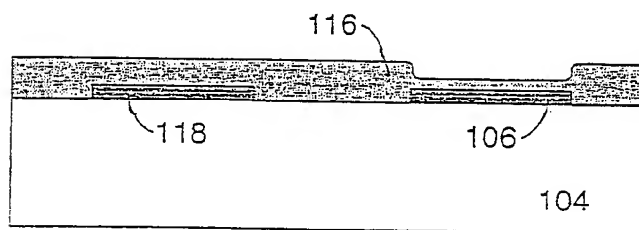


FIGURE 11



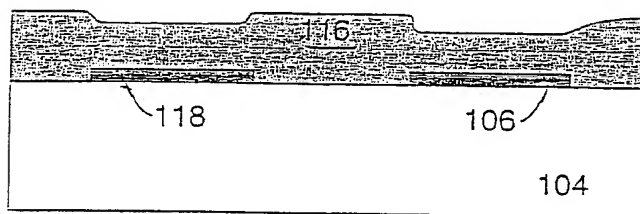
1200

FIGURE 12a Prior Art



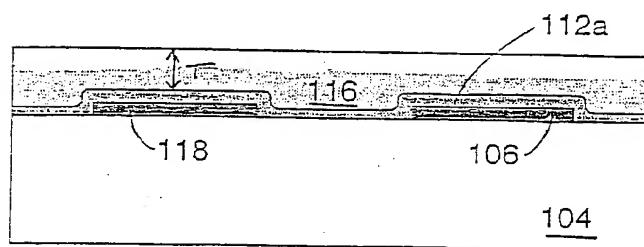
1200

FIGURE 12b Prior Art



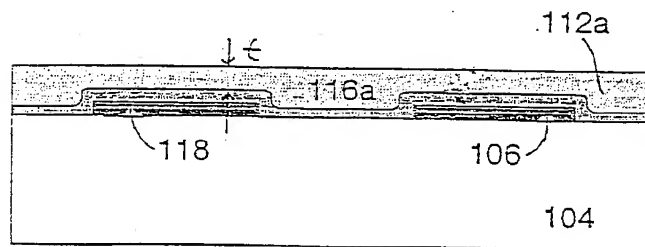
1200

FIGURE 12c Prior Art



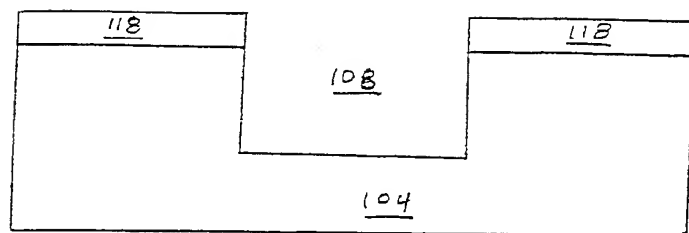
1300

FIGURE 13



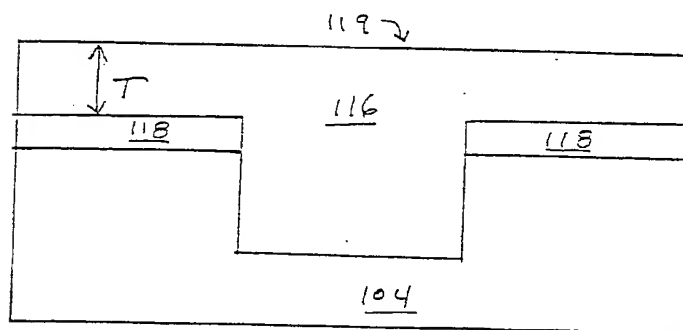
1400

FIGURE 14



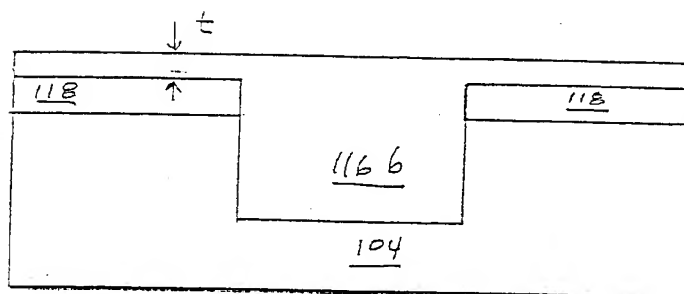
1500

FIGURE 15a



1500

FIGURE 15b



1500

FIGURE 15c



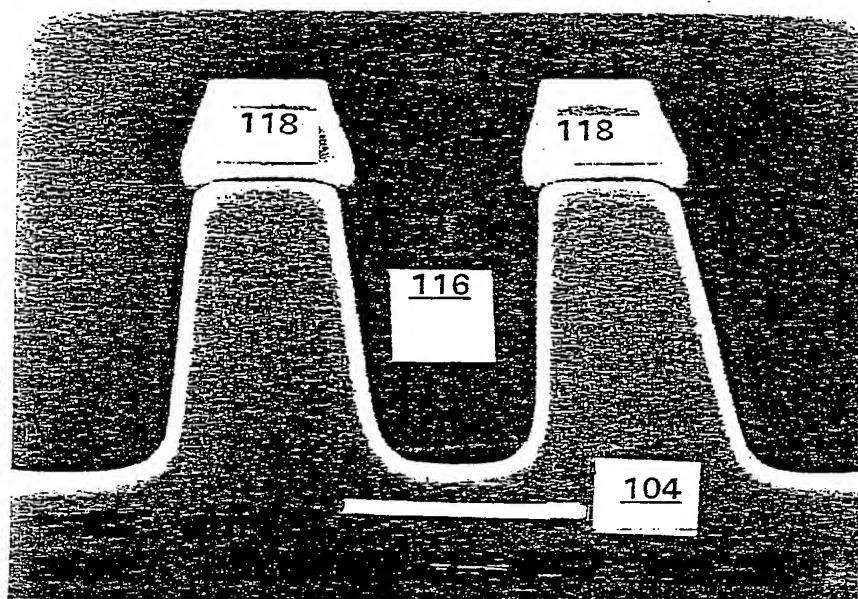


FIGURE 16a

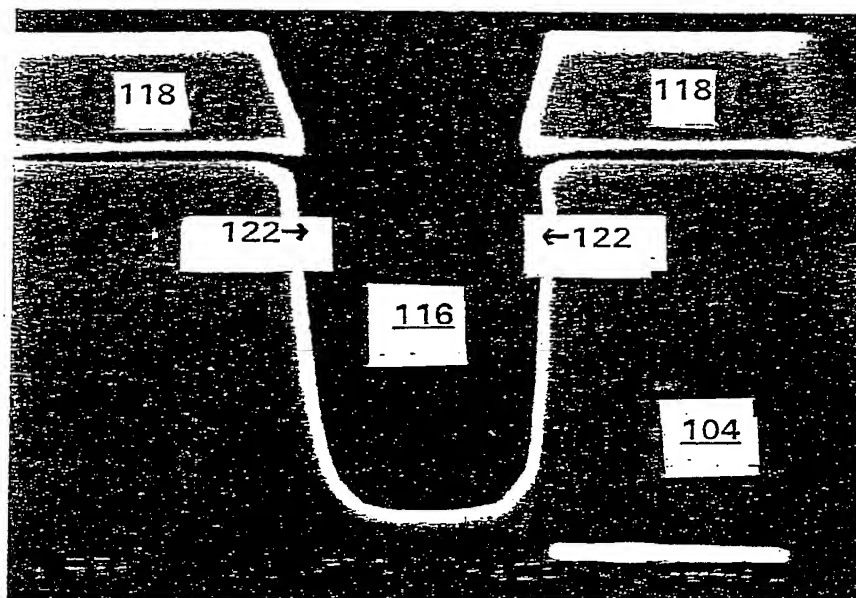


FIGURE 16b

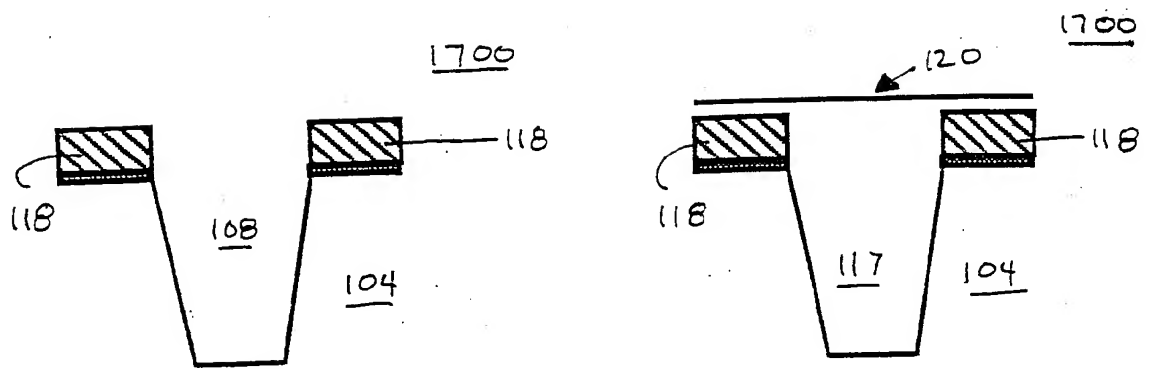


FIGURE 17a

FIGURE 17b

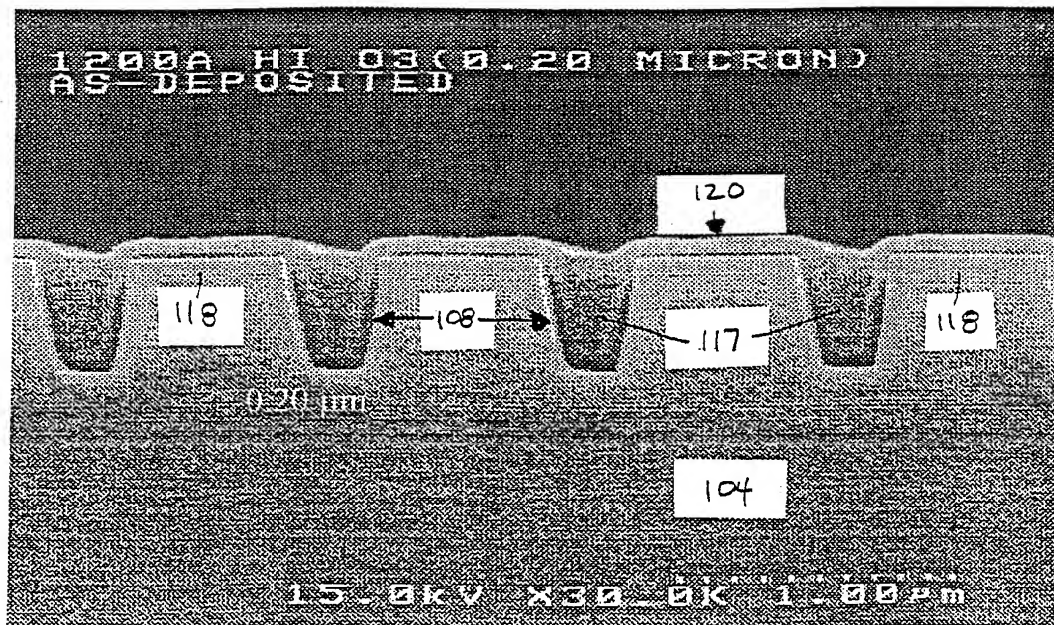


FIGURE 18